AN INVESTIGATION OF THE STRUCTURE OF POLYACRYLONITRILE

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Master of Arts

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by

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CHAPTER I

THE PROBLEM AND ITS IMPORTANCE

I. INTRODUCTION

In the past, many physical and mechanical properties have been measured on films and fibers of polyacrylonitrile. Simultaneously, structural investigations were made on the basis of certain conclusions and assumptions resulting from these studies, and a tentative structural model was proposed. Although there was disagreement as to the type of crystalline unit cell for polyacrylonitrile, it was generally assumed or concluded that polyacrylonitrile consisted of a two-phase order-disorder structure in which the polyacrylonitrile molecule has a regular syndiotactic configuration which is extended in a planar zig-zag chain conformation (21). Neighboring chains were considered to be held together by intermolecular forces of the hydrogen-bonding type. The application of this model to explain the physical and mechanical behavior of films and fibers of polyacrylonitrile resulted in utter failure. The formulation of a new model (3) met with better success in correlating the structure with physical and mechanical properties of polyacrylonitrile. According to the new model, polyacrylonitrile is a single phase structure in which strong intramolecular dipolar repulsions cause a random twisting and distorting of the chain to produce a kinked conformation.

II. THE PROBLEM

It was the purpose of this study (1) to investigate the sorption of N,N-dimethylformamide, DMF, by polyacrylonitrile fibers and films and correlate the observations with its structure; (2) to determine the type of intermolecular forces existing in polyacrylonitrile; (3) to study changes in the structure of polyacrylonitrile, PAN, as a function of the temperature; (4) to employ kinetics of iodine sorption for determining the structure and intermolecular forces existing in polyacrylonitrile; and (5) to correlate all the information obtained with the new structural model.

III. IMPORTANCE OF THE STUDY

It is well known that the physical and mechanical behavior of polymeric systems depend importantly upon the physical structure of the polymer. It is of utmost importance, therefore, to characterize this structure.

Thermal, mechanical, and solvent treatments often effect very significant changes in this structure and simultaneously produce corresponding changes in the physical properties of the system. In many of these cases, such subsequent treatments bring about improvement of the physical and mechanical properties.

CHAPTER II

REVIEW OF THE LITERATURE

Many articles have been written concerning the structural (2, 8, 10, 21, 23, 24, 27, 28), mechanical (3, 21, 27), and thermal (3, 6, 8, 10, 24, 26, 27, 28) properties of polyacrylonitrile. Some of the early literature contain incorrect assumptions and false conclusions (21). Some of the later works (3, 6, 8, 10, 24, 26, 28) are more closely related to the newly proposed structure and the problem being studied.

THE GENERAL PREPARATION, STRUCTURE, AND NATURE OF POLYACRYLONITRILE

Polyacrylonitrile is a member of a group of chemical substances known as polymers. A polymer is made up of structural units repeated many times.

Polyacrylonitrile is usually prepared by the addition polymerization of acrylonitrile, $CH_2=CH-C\equiv N$, in a dispersed system by free radical initiation. The products consist of a heterogeneous mixture ofmolecules having molecular weights which vary continuously from small to very high values.

The physical and chemical properties of such materials depend on the nature of the atoms or molecules constituting them, the location of the molecules with respect to each

other, and the type of interactions within and between the long chain-like molecules.

In polyacrylonitrile, long chain-like molecules are produced by the formation of primary valence bonds of great energy between the carbon atoms constituting the chain. In turn, the molecular chains are held together by variable secondary forces which are much weaker. In polyacrylonitrile these secondary bonds join the long chain molecules laterally. Due to the variability of the secondary bonds, certain chemical and physical properties of the material such as melting point, rate of solution, and extensibility, are determined by these forces. These properties are often dependent upon the methods of preparation and treatment of the polymer. Therefore, by use of thermal and mechanical treatments, it is possible in many cases to modify the material to give it more desirable properties.

THE MICELLE CONCEPT AND ITS RELATION TO THE STRUCTURE AND PROPERTIES OF POLYMERS

According to the micelle concept, a two-phase concept, there are certain regions in the structure where the chain molecules are aligned with respect to each other at definite well-defined distances. These constitute the crystals or the crystallites which are ordered in three dimensions. Also, according to this concept, there are other regions which possess no order at all. These regions are known as

the amorphous zones.

Until recently, it had been assumed that all polymeric materials had structures which were made up of crystalline, or ordered, and amorphous or disordered zones. A more recent study of polytrifluoroacetate and polyacrylonitrile (3) suggest that all polymers do not possess this structure. The two-phase concept has been very useful in explaining the physical and chemical behavior of polymers such as polyethylene terephthalate, 66 nylon, polyethylene, stereoregular polypropylene, and cellulose because these materials show three-dimensional ordered regions and amorphous zones.

All polymers exhibit properties such as physical, and mechanical behavior which are very closely related to the type of order-disorder structure possessed by the polymer. Since the type of order-disorder structure determines these properties, one may alter the properties of polymers by changing the order-disorder structure of the polymer. Thus, a given method of preparation and treatment would produce a certain type of order-disorder structure exhibiting physical properties explainable in terms of the order-disorder structure. For example, if fibers or films of nylon are treated thermally and then annealed, the ordered or crystalline regions might increase, while the force necessary to rupture would decrease, and the sorption of dye and solvents would decrease (28) in proportion to the change in the

order of the structure. The results of such changes serve as a basis upon which physical properties may be justly correlated with the two-phase concept.

To completely assess this order-disorder system it is necessary to have a knowledge of the nature of the molecular chain unit, chain configuration, conformation, the nature of the primary and secondary bonds, and finally, the nature of the ordered regions.

Several tools are employed for the elucidation of such structural problems. X-ray diffraction, infrared spectroscopy, and other optical methods may provide information concerning the conformation, the nature and amount of crystalline regions, and the nature of secondary bonds in polyacrylonitrile.

It is well known that 66 nylon sorbs phenol from mixtures of phenol, a good solvent, and cyclohexane, a non-solvent, and swells (15). Also, there is a concentration of the amorphous halo in the X-ray diffraction pattern (3). The second order transition temperature, Tg, is associated with the disordered regions. Secondary bonds of the hydrogen bond type are present (13). In addition, longitudinal order can be induced by rolling, stretching, and thermal annealing treatments (1). These phenomena are all consistent with the two-phase structure.

APPLICATION OF THE MICELLE CONCEPT TO THE STRUCTURE OF POLYACRYLONITRILE

Most of the information concerning the physical and mechanical properties of polyacrylonitrile fibers and films has been obtained in the last fifteen years. In order to explain the observed properties, it was necessary to determine the structure of the polymer. In characterizing the structure of polyacrylonitrile, false assumptions and conclusions were drawn (21). It was assumed that the structure of polyacrylonitrile adheared to the micelle concept because it had proven quiet successful in characterizing structures of many other polymers. This assumption greatly increased the difficulty of the problem.

The early research was done by using X-ray diffraction and infrared spectroscopy (4, 9, 12, 21, 22, 27). Due to the diffused nature of the X-ray diffraction pattern, a wide variety of interpretations concerning the crystalline and amorphous nature of the material (9, 21, 22, 27), the chain conformation (21), and configuration (21, 27), and the type of intermolecular bonding (21) were fallaciously concluded (3).

Although little information concerning the structure of polyacrylonitrile was valid, the work did reveal the difficulty of the problem of establishing the structure of polyacrylonitrile. Also, it stimulated further research

which led to fruitful and new approaches to the problem.

The unusual nature of polyacrylonitrile was responsible for the false conclusions drawn by the early investigators. Structural studies of order-disorder systems depend on the ability to effect variations in the system by preparatory conditions, thermal, and mechanical treatments. In other polymers, such variations lead to different order-disorder systems, but in polyacrylonitrile little or no structural change can be produced (9, 21, 26, 27).

The physical behavior of polyacrylonitrile differs in many respects from that of the normal crystalline polymers. Films and fibers of polyacrylonitrile do not absorb N,N-dimethylformamide from mixtures of N,N-dimethylformamide, a good solvent, and carbon tetrachloride, a non-solvent. Such behavior is not observed in 66 nylon (15). This suggests the absence of amorphous regions for sorption in polyacrylonitrile which are present in 66 nylon.

The analysis of X-ray diffraction patterns (3) of films and oriented fibers of polyacrylonitrile shows a diffuse pattern with discrete diffraction corresponding to definite lateral packing of the chains. No discrete diffraction corresponding to longitudinal order is present. This indicates the absence of three-dimensionally ordered crystalline regions in the polymer. It was concluded from an analysis of the discrete diffraction that the chains are

packed together in a hexagonal arrangement in which the nearest neighboring chains are 6 Å away.

The diffuse scattering, which is over the major portion of the diagram, appears to be a type of disorder which is very differnt from that in 66 nylon. This implies that there are no amorphous regions in polyacrylonitrile. In normal polymers, thermal and mechanical treatments are used to alter the crystallinity of the polymer, but this is not the case with polyacrylonitrile. The scattering in the X-ray pattern is altered very little by such treatments (26) and no treatment has been successful in imparting longitudinal ordering (3) in polyacrylonitrile.

By use of X-ray and dilatometric data (3), it was possible to determine the cubical coefficient of expansion for polyacrylonitrile. Within experimental error of measurment, it was found to be the same in both cases. This suggests that the cubical coefficient of expansion for the ordered regions is the same as that for the entire polymer. Thus, polyacrylonitrile is composed entirely of this ordered regions, and contains, therefore, no amorphous zones.

Analysis of these data present a very interesting point. The polymer exhibits a transition temperature, Tg, of about 85°C (3, 11). The transition temperature, Tg, has been associated with the amorphous regions in normal crystalline polymers, but in the case of polyacrylonitrile,

it must be associated with the ordered regions.

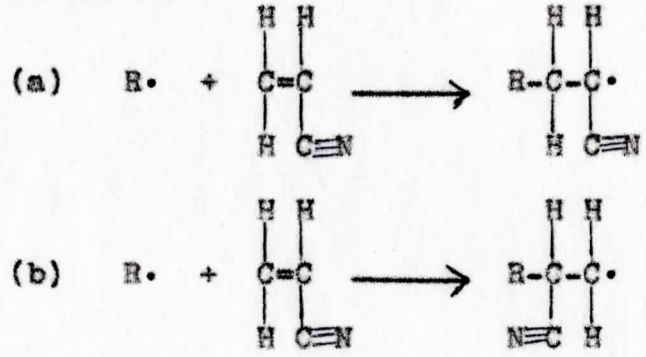
On the basis of this information, the structure of polyacrylonitrile can not be represented by a two-phase fringe micelle structure. Due to the nature of ordered material in the polymer, it appears to be a single phase having a structure somewhere between those of three-dimensional, crystalline material, and disordered, amorphous material.

AN ANALYSIS OF THE DIFFERENT TYPES AND NATURE OF BONDS, CONFORMATION AND CONFIGURATION IN POLYACRYLONITRILE AND THEIR CORRELATION

Bohn (3) used the combined results obtained from X-ray diffraction and infrared spectroscopy studies as a basis for proposing a new chain model for polyacrylonitrile. This model was a single phase ordered structure. Before giving this model it will be useful to review the nature of the bonds, configuration, and conformation.

Vinyl polymers consist of a chain of carbon atoms which serve as the backbone of the molecule. Each carbon atom in the chain is separated by a distance of 1.54 $\mathring{A}$, and the angle between the successive carbon atoms is 110°. To these carbon atoms are attached other atoms or groups of atoms. In polyacrylonitrile half of the carbon atoms are bonded with one hydrogen atom and one nitrile group, (C≡N). The chains may have a fully extended planar, a folded, a kinked, or a helical conformation.

In the polymerization process, there are an infinite number of ways for the succession of the monomer units. A head to tail succession would lead to a regular (isotactic or syndiotactic) structure. On the other hand, a head to head succession would lead to a random alternation (atactic) structure. At this point, two possible mechanisms of initiation will be considered.

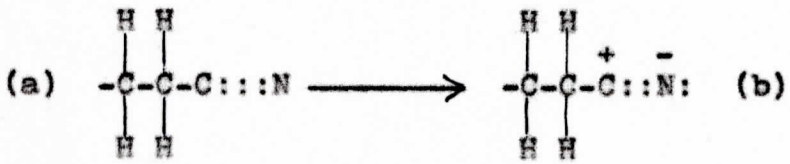


The unpaired electrons in the nitrile group participate in stabilizing the free radical formed in mechanism (a). This mechanism should lead to the predominance of a regular structure (21) which is characteristic of a head to tail arrangement. In support of this, Marvel (14) asserts that vinyl polymers are predominantly of the regular head to tail type. On this point, it is not possible to make a definite conclusion as to whether the configuration is a regular isotactic or syndiotactic, or the irregular random atactic configuration (3, 4, 9, 12, 21, 22, 27). In mechanism (b) the stabilization of the free radical by the unpaired electrons in the nitrile group is much less than the stabilization in mechanism (a).

Primary valence bonds. The carbon chain of the polyacrylonitrile molecule and the atoms and groups attached to it are joined by primary valence bonds. The bonds can be ionic as in NaCl (5) or covalent as in H_2 (5). In many cases the bond is neither of these two extremes, but rather, is an intermediate between the two. This type of bond is demonstrated by the nitrile group.

Secondary valence forces. Polymer films and fibers have their chain molecules united to each other laterally by secondary bonds. In polyacrylonitrile these bonds are electrostatic in nature and are brought into play between groups of an ionic nature.

In the chain molecule of polyacrylonitrile the C-H and C-C bonds are directed covalent bonds (5) with only four percent and zero percent ionic character (5), respectively. Due to the unshared electrons in the nitrile group, resonance structures of the type (a) and (b) are possible. In this case, the nitrile group possesses an ionic structure as follows:



The degree to which the ionic structure contributes is shown by the high dipole moment of the nitrile group. According to Pauling (19), the two structures contribute almost equally.

Secondary bonds of an electrostatic type are either hydrogen bonding or dipolar. In order to establish the probable chain conformation in polyacrylonitrile, it is necessary to decide which type of secondary forces are brought into play.

Hydrogen bonding. The solubility of polyacrylonitrile in solvents of high dipole moments, such as N,N-dimethylformamide and dimethylsulfoxide, has been used as a basis for assuming the existence of hydrogen bonding (20). This, however, is not sufficient reason to consider the assumption valid. Usually, hydrogen bridges are formed only between highly electronegative atoms, such as fluorine, oxygen, and nitrogen. From Figure 1, one can see that in polyacrylonitrile it is necessary for the hydrogen atom to bridge a nitrogen of one chain molecule to the carbon of an adjacent chain molecule. In this case, the nitrile group is quite ionic while the C-H of the other chain molecule is only very slightly ionic. In one case, a hydrogen does bridge a carbon to an oxygen atom (5), but in this case, the C-H bond exhibits a much greater ionic character. On the basis of X-ray investigation (9, 17, 21) and infrared spectroscopy (21), the results have been inconclusive.

Dipolar forces. If secondary forces are brought into play by the nitrile groups between neighboring chains, it might be expected that dipolar repulsions would arise. The nitrile groups would try to move as far from each other

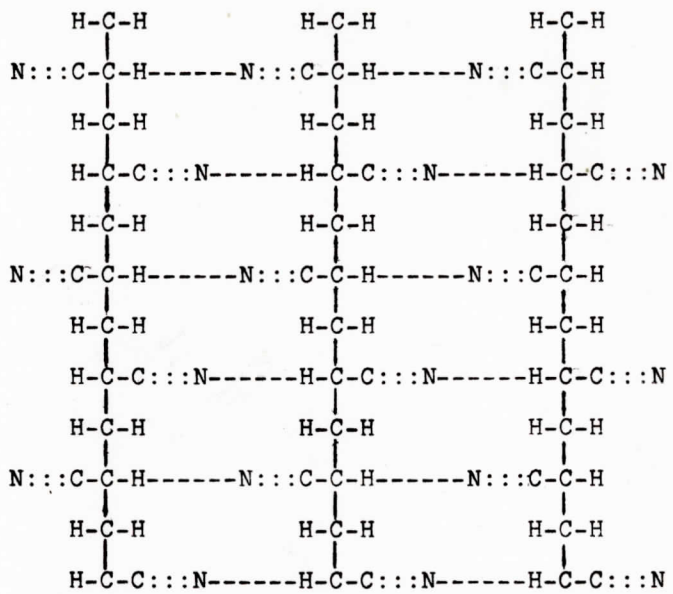


FIGURE 1

THE TYPE OF BOND NECESSARY FOR HYDROGEN BONDING
IN POLYACRYLONITRILE

as possible. Such repulsions could cause the chain of carbon atoms to assume some sort of twisted or distorted conformation. Infrared spectroscopy studies (21) were not able to establish conclusively the existence of dipolar type secondary forces. However, on the basis of the sorption characteristics and the single phase concept, it seems valid to assume that hydrogen bonding secondary forces do not exist in polyacrylonitrile. Further evidence for this assumption is given by the studies made by Bohn (3) using X-ray diffraction and polarized infrared radiation. From a comparison of the infrared dichroic ratios of the C-H and CN stretch, it was concluded that the chain conformation is not a fully extended planar zig-zag chain. From a combination of the results of these investigations, Bohn (3) proposed the following structural model for polyacrylonitrile:

BOHN'S PROPOSAL OF A NEW CHAIN MODEL FOR POLYACRYLONITRILE

The polyacrylonitrile chain molecule is pictured as a randomly kinked chain conformation. Such a chain conformation occurs because of the close proximity and dipolar character of the nitrile groups. These nitrile groups interact to produce great twisting and distortion, sometimes clockwise and sometimes counterclockwise to produce a randomly kinked chain conformation. This twisting would be expected to occur no matter what the chain configuration. This

twisting force is opposed only by the primary valence bond forces along the polymer chain. In the final kinked molecule there is a delicate balance between the dipolar repulsions and the opposing primary valence bond forces. This chain is contained in a more or less symmetrical cylinder with an average diameter of 6 Å.

Because of the twisting and distortion, the CN groups make a distribution of different angles to the cylinder axis. This conformation is consistent with the low dichroic ratios, low birefringence, and lack of longitudinal order (3).

Molecular models show that the stiff kinked polyacrylonitrile chain can not fit completely within the 6 Å diameter cylinder unless some of the nitrile groups stick out beyond the confines of the cylinder. These CN groups which stick out are potentially available for intermolecular bonding. The dipolar bonding in simple nitriles is about as effective in raising the boiling point as hydrogen bonding in alcohols (25).

In polyacrylonitrile, optimum pairing of the nitrile groups can not occur because of the many directions in which the CN groups stick out due to the random kinking of the chain. This implies that weak intermolecular forces exist between the cylinders. This is consistent with Krigbaum's conclusions from enthalpy data (11) and the tendency of

oriented films to readily fibrillate (3).

These stiff cylinders pack laterally into an hexagonal arrangement so as to produce a single phase polymer structure having properties intermediate between those of crystalline and amorphous material.

Thermal treatment or mechanical treatment may modify slightly the intermolecular forces and hence the conformation, but the controlling forces are the much stronger intramolecular dipolar secondary forces. This is consistent with the inability to effect changes in the intermolecular forces by preparatory methods (3), heat, and mechanical treatments (3, 4, 9, 21, 22, 27).

THE THEORY OF SORPTION AND ADSORPTION

SORPTION

Sorption is a term used to describe the fact that a component has moved form one phase to another, particularly when the other phase is a solid (17). For example, if a film of polyacrylonitrile is placed in an aqueous solution of potassium iodide containing iodine, the iodine moves from the solution to the polyacrylonitrile. We can say that the polyacrylonitrile has sorbed the iodine. The iodine is called the sorbate. In this case, if it can be established that the iodine is only on the surface of the polyacrylo-

nitrile, then we speak of adsorption (17). If on the other hand, the iodine is distributed throughout the entire internal structure of the polymer, then we speak of absorption (17).

It is not always easy to establish whether sorption is an adsorption or absorption process. This is especially true when solubilization occurs. For example, benzene is nearly insoluble in water, but dissolves markedly in solutions of association colloids such as sodium lauryl sulfate. It is found that the solubility of benzene is almost directly proportional to the concentration of the micelles. The micelles sorb the benzene and thus hold it in solution. Whether the process is adsorption or absorption must be based primarily on the nature of the micellar structure (17).

ADSORPTION

Adsorption may result when there are attractive forces between the sorbate and sorbent particles. These attractive forces may be of a van der Waal's type or of a chemical nature.

Adsorption is classified as physical adsorption or chemisorption, depending on the type of bonding formed between the adsorbate and adsorbent (17). Often different types of forces combine to cause adsorption, consequently it is not always easy to decide whether the adsorption is physical or chemisorption. Physical adsorption is described

as surface condensation, and chemisorption as surface reaction.

For adsorption to occur, the adsorbate must reach the sorbent and attach itself, at least for a short time. The rate at which sorbent is reached will depend on the concentration of the sorbate (17), and the rate of Brownian motion of the sorbate particle (17).

The number of particles with diffusion coefficient D and concentration c which will reach a unit surface in time t is given by (17):

$$n = \tfrac{1}{2}c\sqrt{2Dt}$$

For aqueous solutions, n is large. For a 0.1% by volume aqueous solution of particles with a radius of 10 Å, enough solute will reach a surface in ten seconds to build up a layer 1000 Å thick (17).

If there are no attractive forces between adsorbate and sorbent, no attachment to the surface is expected and equilibrium is quickly established. Also, if attractive forces are established all along as sorbate approaches the sorbent, equilibrium is quickly established.

In chemisorption, there is no or only weak interaction unless the sorbate and sorbent are brought together with great force and energy. When this occurs, a very strong bond is formed. In other words, the reaction between sorbate and sorbent may be slow and require a large activation energy.

Of the many particles which reach the surface and attach to it by van der Waal's forces, only a very few may acquire enough energy by random collisions to become chemisorbed. The rate of reaching equilibrium with respect to chemisorption may be very slow or even negligible under such circumstances. It will be greatly effected by increased temperature, however. This is called activated chemisorption.

Activated adsorption on an accessible surface is always chemisorption, but chemisorption may be either simple or activated.

The situation on a surface depends greatly on the amount adsorbed. If the amount adsorbed is very low, the few sorbate particles are far away from each other. As the amount sorbed increases, sorbate-sorbate interactions become important. This leads to multilayer adsorption which may or may not precede monolayer adsorption.

CHAPTER III

EXPERIMENTAL INVESTIGATIONS OF POLYACRYLONITRILE

MATERIALS AND EQUIPMENT USED

The materials used for this study are as follows: polyacrylonitrile polymer, oriented polyacrylonitrile fibers, iodine, potassium iodide, N,N-dimethylformamide, ethyl alcohol, carbon tetrachloride, and toluene.

The equipment employed in this study were the following: Hanging Drop microscope slides, glass plates 3" X 3", temperature regulated oven, thermoregulated constant temperature water bath, 125 ml Erlenmeyer flasks, Abbe Refractometer, pycnometer, Bausch and Lomb Polarizing Microscope, illuminating lamp for microscope, Perkin-Elmer Infracord with NaCl optics, Beckman Infrared Spectrophotometer, Model IR-7 with NaCl prism and grating optical elements, and a Perkin-Elmer Heated Cell with NaCl circular windows.

SAMPLE PREPARATION

One percent by weight solutions of polyacrylonitrile in N,N-dimethylformamide were prepared and uniformly poured on the surface of 3" X 3" glass plates. The plates thus prepared were allowed to stand at room temperature until the solvent had partially evaporated. The plates were then placed in an oven whose temperature was controlled at 110^{o}C

for a period of two hours.

It is interesting to observe that on the days when the humidity was relatively high that the polyacrylonitrile precipitated from the dimethylformamide solution as a finely divided white powder. Apparently sufficient moisture is taken up by the solvent to render it enough of a non-solvent to cause some of the polymer to precipitate. This undesirable situation was avoided, however, by placing the prepared glass plates directly into the oven.

The oriented fibers were available for this investigation. Hence, it was not necessary to prepare these.

EXPERIMENTAL PROCEDURES

The experimental study is divided into the following four investigations: (1) study of the sorption of N,N-dimethylformamide by fibers and films of polyacrylonitrile; (2) infrared spectroscopic studies of the existence of hydrogen bonding intermolecular forces in polyacrylonitrile; (3) studies of the intermolecular forces in polyacrylonitrile by a study of the thermal treatment of films; and (4) studies of the sorption of iodine by films of polyacrylonitrile.

THE SORPTION OF N,N-DIMETHYLFORMAMIDE BY POLYACRYLONITRILE FIBERS AND FILMS

This study consisted of (1) a microscopic investi-

gation of the swelling of oriented fibers of polyacrylonitrile and (2) the investigation of the sorption of dimethylformamide from mixtures of dimethylformamide and ethyl alcohol, dimethylformamide and n-propanol, dimethylformamide and carbon tetrachloride, and dimethylformamide and water.

Microscopic investigation. Single filaments of the polyacrylonitrile were placed in the depression of an Hanging Drop microscope slide and brought into focus on the stage of the Bausch and Lomb microscope. These filaments were bathed in dimethylformamide. By using a magnification of 250X, the filaments were continuously observed with respect to their diameter increases or decreases.

Studies by use of refractive index. This study was carried out in an attempt to follow the sorption of dimethylformamide by the polyacrylonitrile filaments. Changes in the refractive index of the various solutions after being in contact with the filaments for different times were measured with an Abbe Refractometer.

Preliminary to this study, dimethylformamide composition versus refractive index curves for dimethylformamide-water mixtures were established. For this curve, mixtures ranging from 0-70% by weight dimethylformamide were employed.

Approximately 0.5 gram of polyacrylonitrile fiber was immersed in 30 ml of the aqueous solutions of dimethylformamide having compositions of 5, 10, 15, 20, 25, 30, 40, 50, 60, and 70 percent by weight dimethylformamide. These

immersions were carried out at 25°C for periods of time ranging from thirty minutes to forty-eight hours. Similar experiments were carried out at other temperatures up to 80°C. These experiments were also carried out with ethyl alcohol, n-propanol, and carbon tetrachloride solutions of dimethylformamide. Refractive indexes were measured for each of these solutions.

Use of infrared spectroscopy. Films of polyacrylonitrile cast from dimethylformamide, as previously described, were used for this study. By means of a Perkin-Elmer Model 137 Infracord with NaCl optics and double beam operation, the infrared spectrum of the polyacrylonitrile film from 2.5μ to 15μ was recorded.

The films were then immersed in the various dimethylformamide-water mixtures, previously described, for forty-eight hours. These films were then wiped dry and similar infrared spectra were obtained. The various spectra were indexed with respect to the CN stretching frequency, the C-H stretching frequency, the C-H bending frequency, and the band at 1675 cm^{-1} associated with the dimethylformamide. In addition, changes in the intensities of these bands were noted.

INFRARED SPECTROSCOPIC STUDY OF HYDROGEN BONDING IN POLYACRYLONITRILE FILMS

In an earlier investigation with orlon, J. J. Point

(21) reported a difference in the infrared absorption frequency of the nitrile, CN, stretch for a polyacrylonitrile film and polyacrylonitrile dissolved in dimethylformamide. The frequency reported for the film was 6.9 cm^{-1} less than that of the solution. This result was not confirmed in a later experiment, however. The shift of frequency observed in the solution was interpreted as being due to intermolecular forces of the hydrogen bonding type. Point's experiment was repeated using a Beckmann IR-7 Spectrophotometer to see if we could observe a shift in the CN stretching frequency for our polyacrylonitrile films and polyacrylonitrile-dimethylformamide solution.

Infrared spectra for both film and solution were recorded with the IR-7 Infrared Spectrophotometer, using conditions of chart speed and scanning speeds which would give maximum resolution. These results were compared with the results reported by J. J. Point.

A STUDY OF THERMAL TREATMENT OF POLYACRYLONITRILE FILMS BY INFRARED SPECTROSCOPY

In many polymeric systems, polyethylene, 66 nylon, and steroregular polypropylene, thermal treatments bring about certain structural changes due to the weakening of the intermolecular forces. Such changes are accompanied by changes in the infrared absorption spectrum.

For this study, a Perkin-Elmer Heated Cell was used.

This cell consists of circular NaCl discs separated by lead spacers. The temperature is detected by means of a thermocouple element placed next to the sodium chloride disks. By means of a potentiometer circuit, the temperature is read from the meter in arbitrary units. These meter readings can be calibrated in terms of degrees centigrade or fahrenheit. By means of this cell, infrared spectra may be obtained at constant temperatures ranging from 25° to 200°C.

In this study, a polyacrylonitrile film was placed between polished NaCl disks separated by a lead spacer. Preliminary spectra of the film were taken at 25°C, 54°C, 82°C, 110°C, 160°C, and 190°C from 2.5u to 15u with the Perkin-Elmer Infracord. These same experiments were repeated with the Beckmann IR-7 Infrared Spectrophotometer. The absorption bands were indexed with respect to position and relative peak intensities.

STUDIES OF THE SORPTION OF IODINE BY FILMS OF POLYACRYLONITRILE

PRELIMINARY STUDIES OF THE SORPTION OF IODINE BY POLYACRYLONITRILE

Preliminary studies on the sorption of iodine by polyacrylonitrile films were carried out by preparing solutions of iodine in ethyl alcohol, iodine in carbon tetrachloride, iodine in water, and iodine in aquious

potassium iodide solutions.

Films were immersed in each of these solutions, in turn, over periods of from thirty minutes to forty-eight hours in a water bath maintained at 40°C, ±0.1°C. These experiments were carried out at higher temperatures also. The films were removed, rinsed with water at 25°C, and the amount of iodine sorbed was estimated by visual obserbation.

The results of these preliminary studies, as will be seen later, show that polyacrylonitrile films sorb iodine only from aqueous potassium iodide solutions.

DETAILED STUDIES OF THE SORPTION OF IODINE BY POLYACRYLONITRILE FILMS

To follow the sorption of iodine, the effects of time, temperature, and concentration of solutions were studied.

Aqueous potassium iodide solutions having concentrations of 2, 4, 8, 12, 16, 20, and 24 grams of iodine per liter were prepared. Fifty milliters of each of these solutions were transferred to Erlenmeyer flasks which were placed in a water bath maintained at various constant temperatures, 34.5, 44.3, 49.7, 55.7, 59.7, and 65°C, by means of a thermoregulated water bath. Polyacrylonitrile films were immersed in these solutions for various periods of time. At specified times, the films were removed, rinsed in water, then dried at room temperature. The dried samples were then weighed, and the percent iodine index, grams of iodine per

hundred grams of polymer, sorbed was obtained.

A STUDY OF THE RATE OF SORPTION OF FILMS AS A FUNCTION OF THE THERMAL TREATMENT

Various polyacrylonitrile films were prepared as previously described. These films were subjected to various heat treatments in an attempt to produce films possessing different densities.

The densities of these films were determined by a flotation method in appropriate mixtures of carbon tetrachloride and toluene.

Each of these films was immersed in a solution of aqueous potassium iodide containing 20 grams of iodine per liter maintained in a water bath at 55.7°C. The films were removed at various times, dried, weighed, and the percent iodine sorbed was determined.

THE DISORIENTING AND SOFTENING OF FIBERS AND FILMS OF POLYACRYLONITRILE BY AQUEOUS I_2-KI SOLUTION

Oriented polyacrylonitrile fibers were placed in a test tube containing an aqueous potassium iodide solution containing 24 grams of iodine per liter. The test tube and its contents were placed in boiling water for approximately fifteen minutes, after which the fibers were removed and observed.

CHAPTER IV

RESULTS AND DISCUSSION OF RESULTS

THE SORPTION OF N,N-DIMETHYLFORMAMIDE BY POLYACRYLONITRILE FILMS AND FIBERS

The oriented filaments bathed in N,N-dimethylformamide were observed under the microscope to dissolve rapidly. No increase in the diameter of the filaments could be detected prior to solution. In fact, a gradual decrease in the diameter is observed. Such behavior is different from that observed when 66 nylon is placed in phenol or mixtures of phenol and water. Here, an increase in the diameter of the filament is observed. This behavior is due to the weakening of the hydrogen bonding intermolecular forces in nylon.

In the case of polyacrylonitrile, it appears that the mechanism of solution is a sorption process. It further appears to indicate weak intermolecular forces.

A plot of the refractive index of the various N,N-dimethylformamide-water solutions as a function of the N,N-dimethylformamide concentration results in a straight line. This data is given in Table I. Figure 2 is a plot of the refractive index versus dimethylformamide concentration.

TABLE I

THE REFRACTIVE INDEX AT 25°C FOR WATER SOLUTIONS OF DMF HAVING VARIOUS COMPOSITIONS BY WEIGHT

Percent DMF	Refractive Index
0	1.3311
5	1.3370
10	1.3430
15	1.3490
20	1.3550
25	1.3611
30	1.3670
40	1.3794
50	1.3912
60	1.4031
70	1.4150

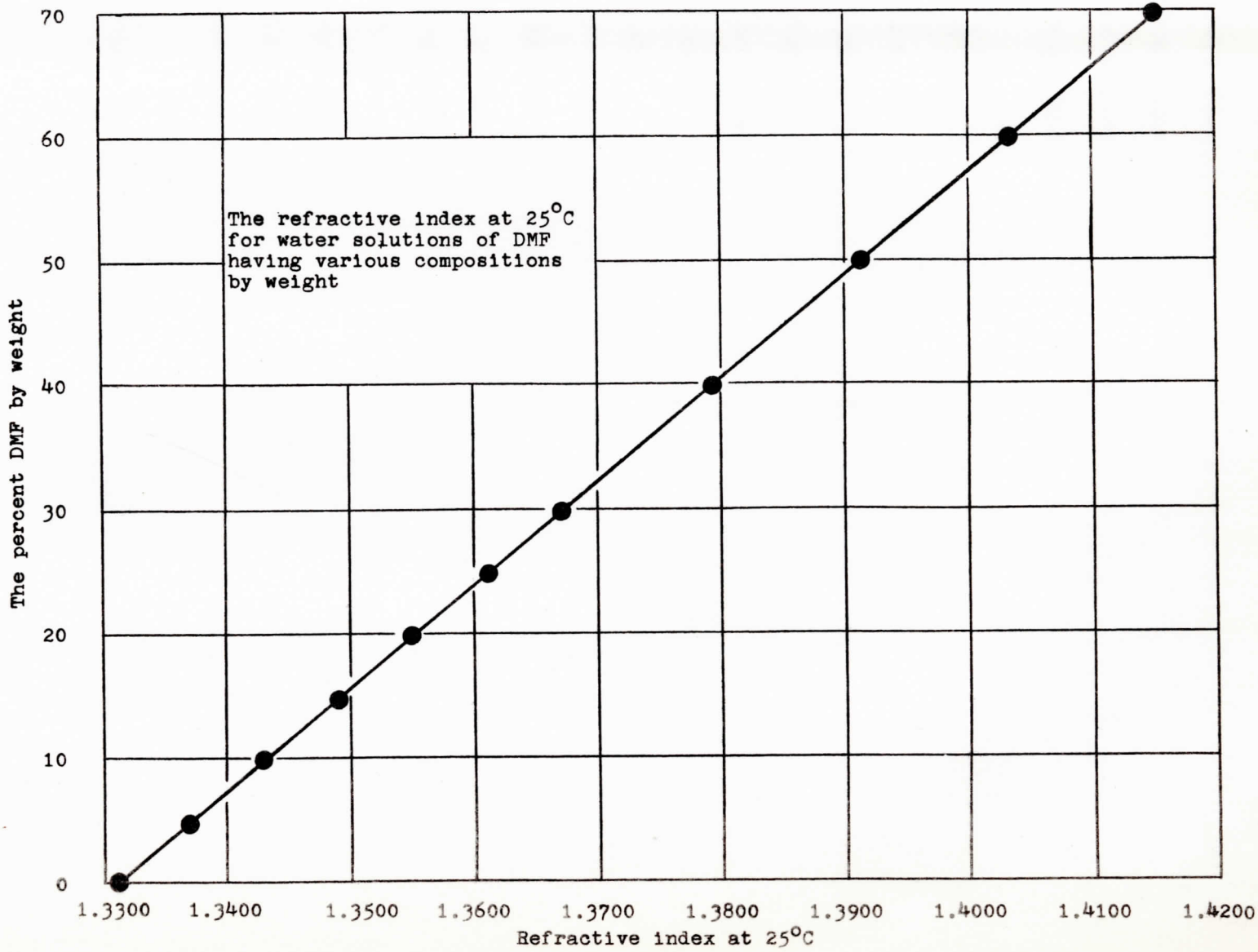

The refractive index at 25°C for water solutions of DMF having various compositions by weight
The percent DMF by weight
0
10
20
30
40
50
60
70
1.3300
1.3400
1.3500
1.3600
1.3700
1.3800
1.3900
1.4000
1.4100
1.4200
Refractive index at 25°C

FIGURE 2

When the various mixtures of dimethylformamide in ethyl alcohol, carbon tetrachloride, n-propanol, and water were measured, it was found that the refractive indexes of the solutions did not change significantly. These results are given in Table II, and are shown graphically in Figure 3.

These results indicate that N,N-dimethylformamide is not sorbed by the polyacrylonitrile fibers from these mixtures. This, again is a behavior at variance with the behavior of 66 nylon toward mixtures of phenol, a good solvent, and cyclohexane, a non-solvent. This result appears to be inconsistent with the behavior to be expected for a polymeric material with intermolecular forces of the hydrogen bonding type.

The infrared spectra for the various films treated with the various aqueous solutions of dimethylformamide show no change in the frequencies or intensities of the nitrile stretching (2275 cm^{-1}), C-H bending (1450 cm^{-1}), and the C-H stretching (2940 cm^{-1}) absorption bands for the polyacrylonitrile. Also, the absorption band at 1675 cm^{-1}, (Figure 4), due to the amide stretching in the dimethylformamide showed no significant change in intensity.

These results show that no dimethylformamide is sorbed by the films from these solutions.

TABLE II

THE CHANGE IN REFRACTIVE INDEX AT 25°C OVER VARIOUS PERIODS OF TIME FOR THREE WATER SOLUTIONS OF DMF IN WHICH 0.5 GRAM OF POLYACRYLONITRILE FIBERS WAS IMMERSED

Time in minutes	Refractive Index		
	(I) 65% DMF	(II) 48% DMF	(III) 24% DMF
0	1.4100	1.3900	1.3600
60	1.4100	1.3900	1.3600
120	1.4100	1.3900	1.3600
180	1.4100	1.3900	1.3600
240	1.4100	1.3900	1.3600
300	1.4100	1.3900	1.3600
360	1.4100	1.3900	1.3600
420	1.4100	1.3900	1.3600
480	1.4100	1.3900	1.3600

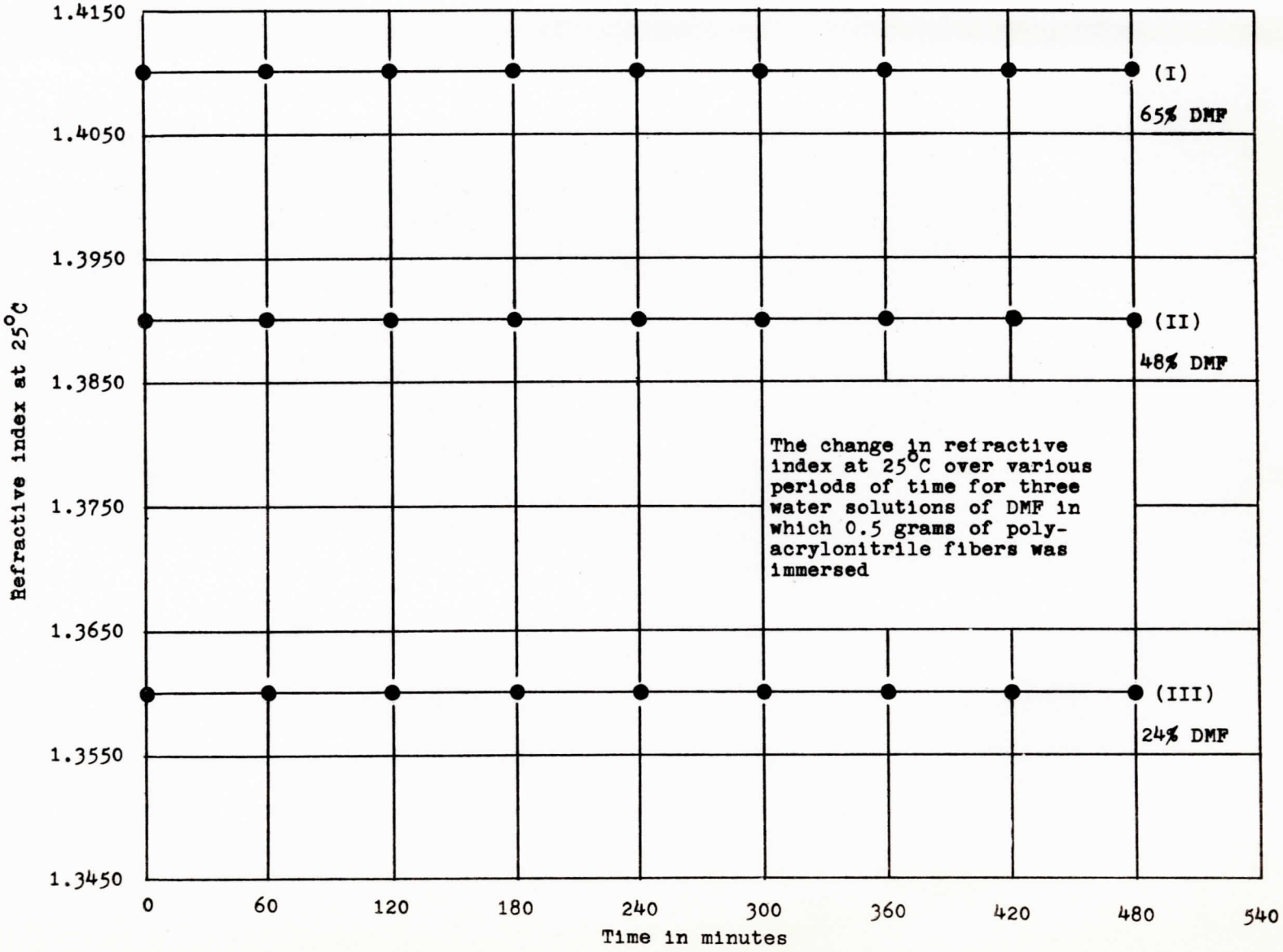

1.4150
1.4050
1.3950
1.3850
1.3750
1.3650
1.3550
1.3450
Refractive index at 25°C
0
60
120
180
240
300
360
420
480
540
Time in minutes
(I)
65% DMF
(II)
48% DMF
(III)
24% DMF
The change in refractive index at 25°C over various periods of time for three water solutions of DMF in which 0.5 grams of poly-acrylonitrile fibers was immersed

FIGURE 3

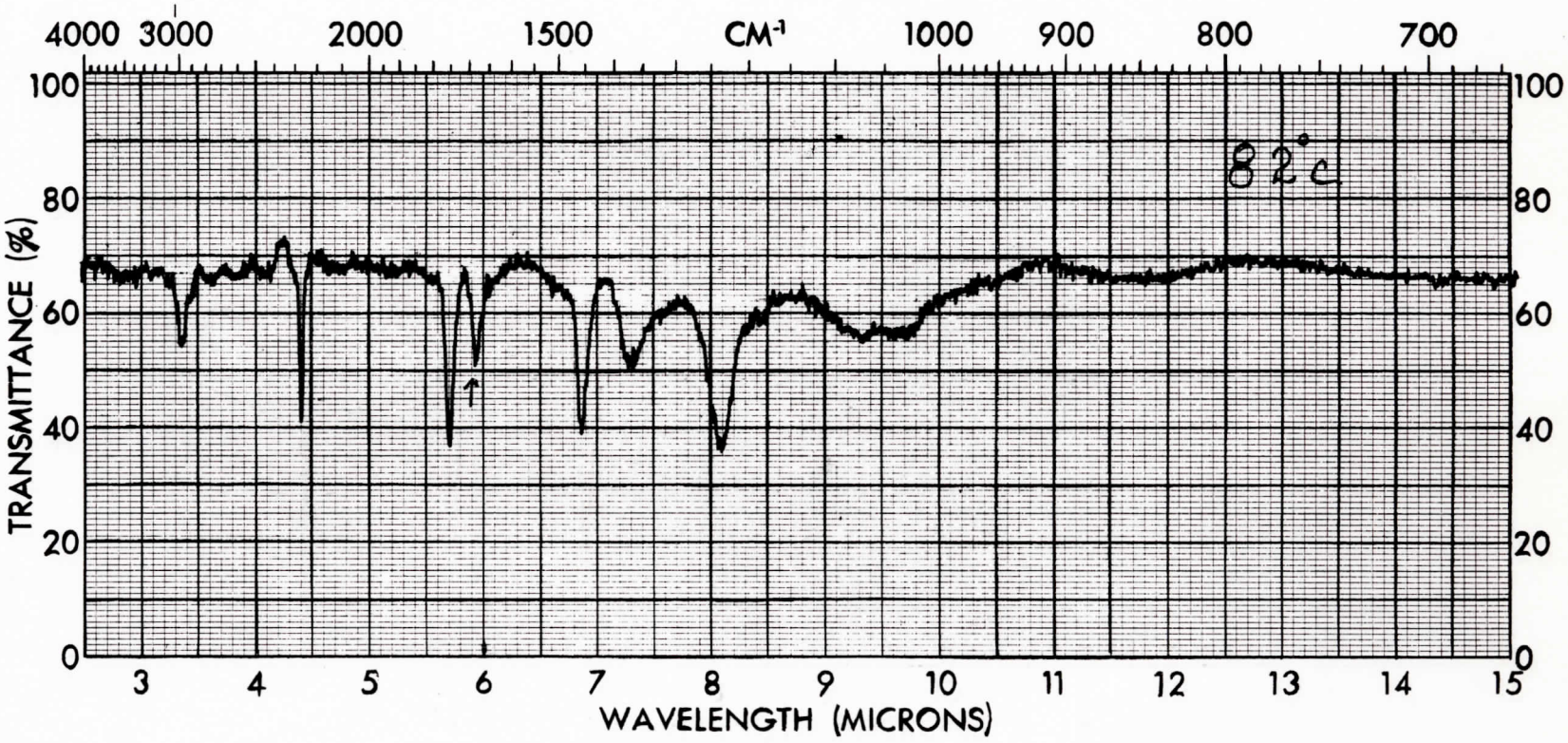


FIGURE 4

AN INFRARED SPECTRUM OF A POLYACRYLONITRILE FILM WHICH EXHIBITS A BAND AT 1675 Cm^{-1} WHICH IS DUE TO THE PRESENCE OF N,N-DIMETHYL FORMAMIDE

INFRARED STUDIES OF POLYACRYLONITRILE FILMS AND POLYACRYLONITRILE-N,N-DIMETHYLFORMAMIDE SOLUTIONS

The studies of the infrared absorption of the CN stretch for solution and film with the IR-7 Spectrophotometer gave a value of 2243 cm^{-1} for both solution and film. Thus, no shift such as that reported by J. J. Point is observed. It may be noted also, that Point gives for this frequency a value of 2293 cm^{-1}. This difference may be due to the use of an instrument of poorer resolution by Point.

These results are shown in Figure 5. It appears, on the basis of these results, that the assumption of hydrogen bonding is not valid.

INFRARED STUDIES OF POLYACRYLONITRILE FILMS AT DIFFERENT TEMPERATURES

The position and the intensities of the nitrile stretch, the C-H stretch, and the C-H bending frequencies were obtained for the film at temperatures of 30°C, 75°C, 130°C, 155°C, and 195°C. No significant changes in the frequency or peak intensities were observed up to 195°C. See Figures 6, 7, 8, 9, and 10. The thermal behavior of polyacrylonitrile is very different from that of polyethylene, 66 nylon, and polyethylene terephthalate in which there are drastic changes in both position and intensity of absorption bands due to weakening of the intermolecular forces.

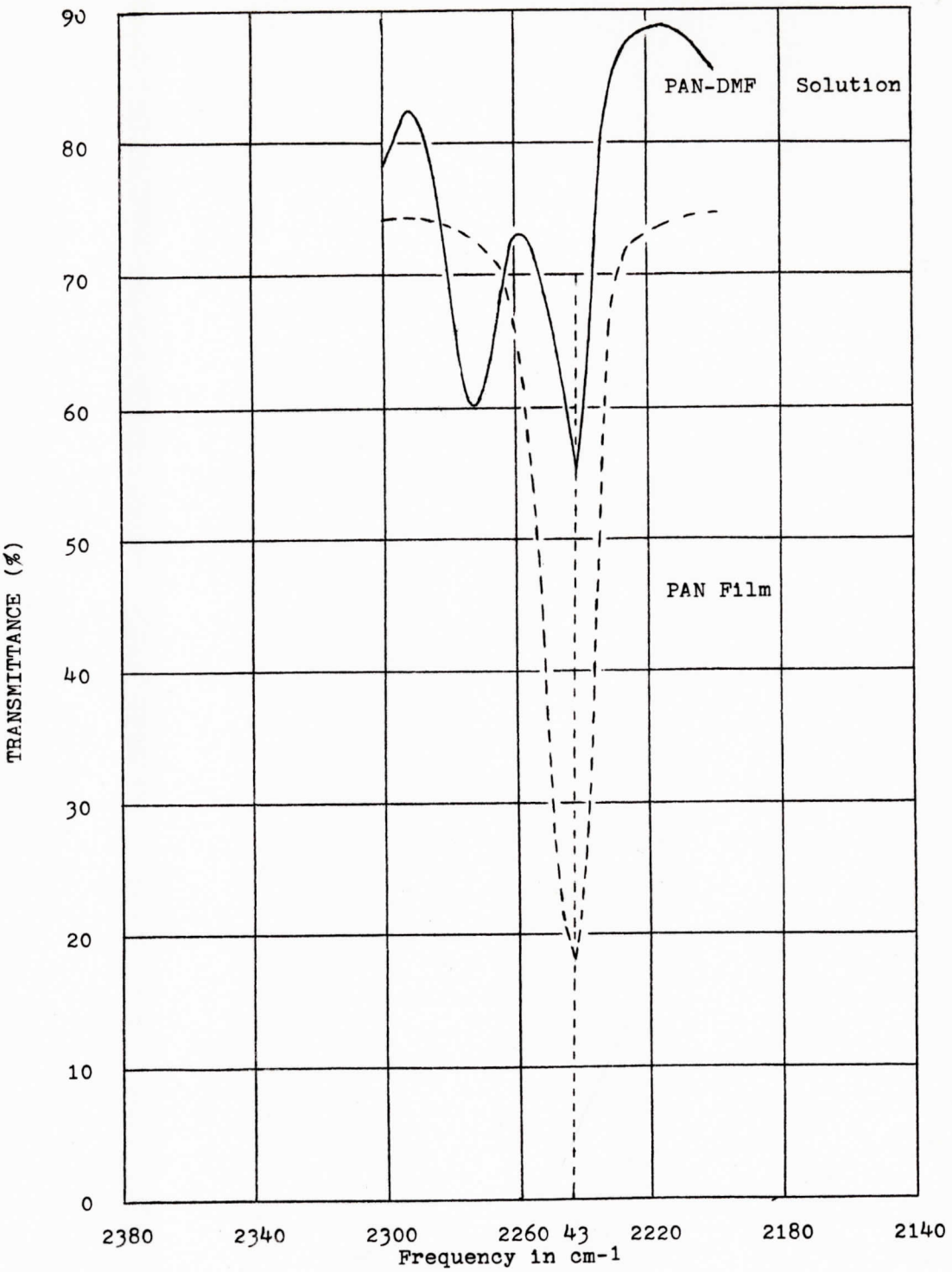


FIGURE 5
INFRARED SPECTRA OF DMF-PAN SOLUTION AND PAN FILM

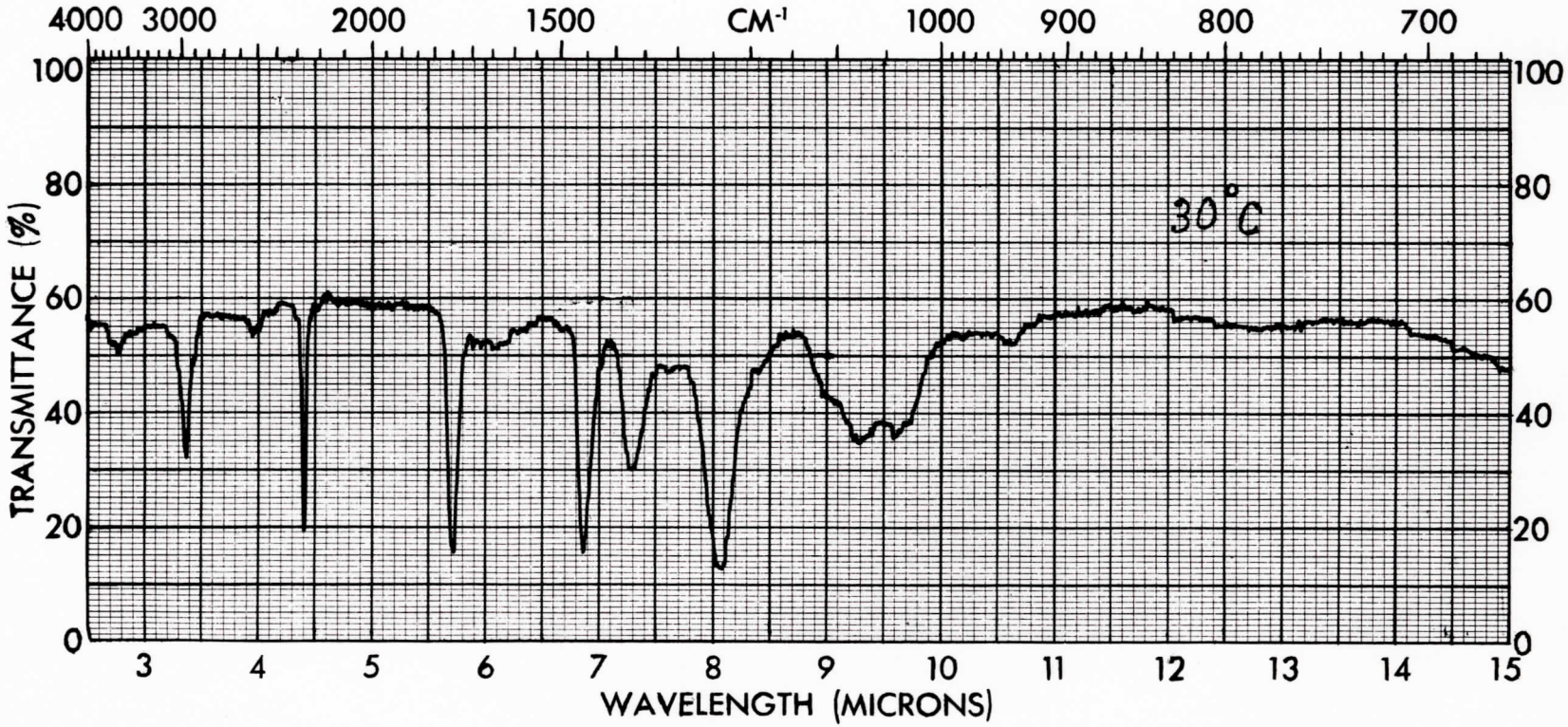


FIGURE 6

THE INFRARED SPECTRUM OF POLYACRYLONITRILE OBTAINED WITH A PERKIN-ELMER INFRACORD, MODEL 137 AT 30°C

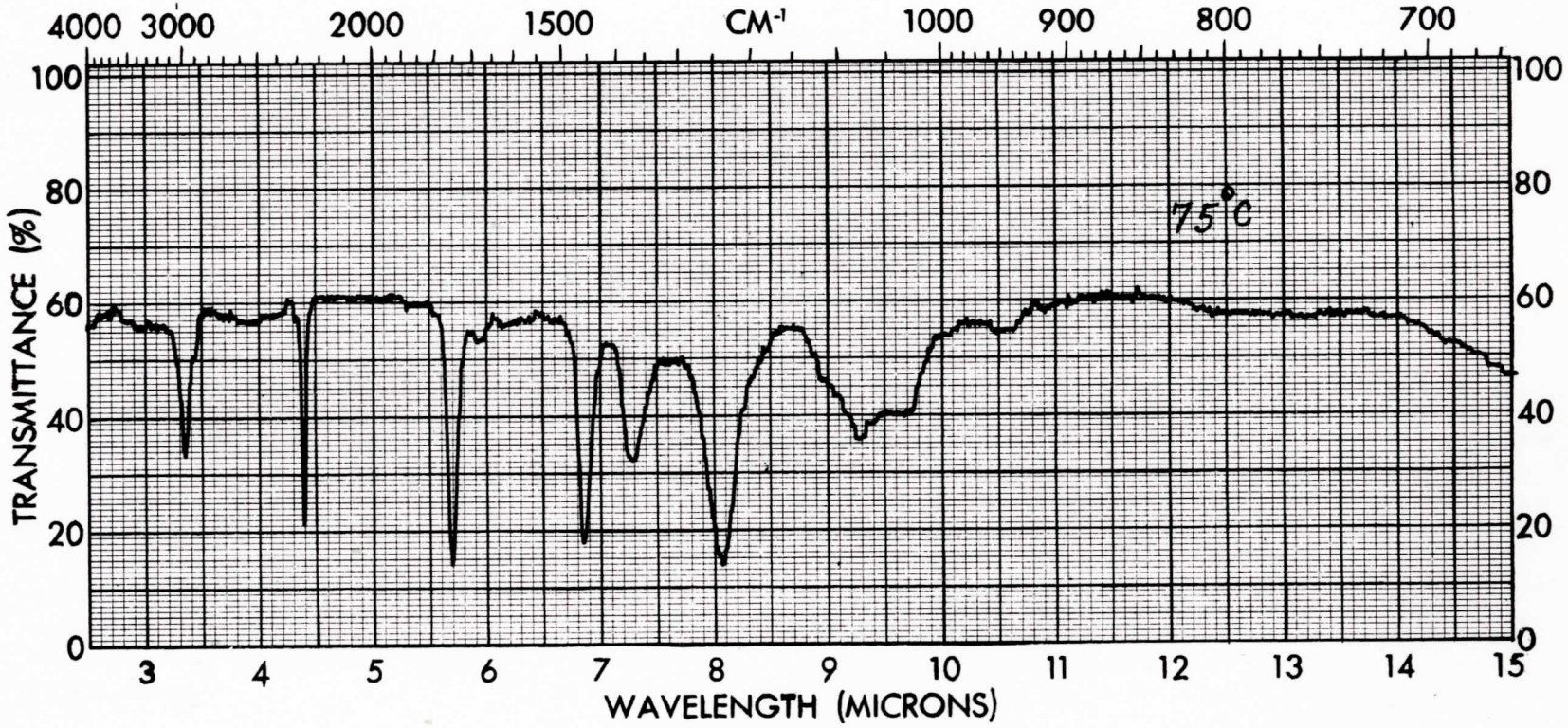


FIGURE 7

THE INFRARED SPECTRUM OF POLYACRYLONITRILE OBTAINED WITH A PERKIN-ELMER INFRACORD, MODEL 137 AT 75°C

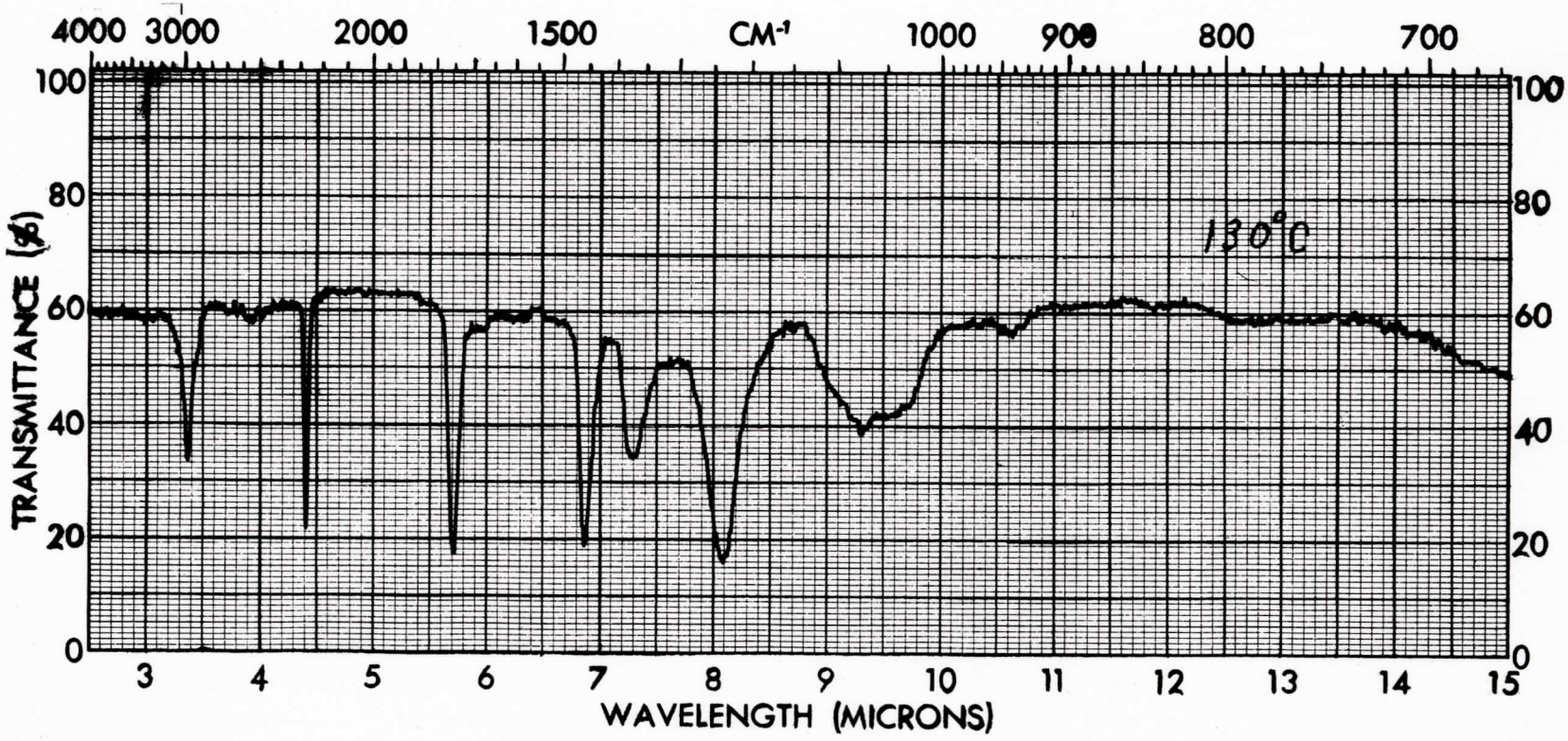


FIGURE 8

THE INFRARED SPECTRUM OF POLYACRYLONITRILE OBTAINED WITH A PERKIN-ELMER INFRACORD, MODEL 137 AT 130°C

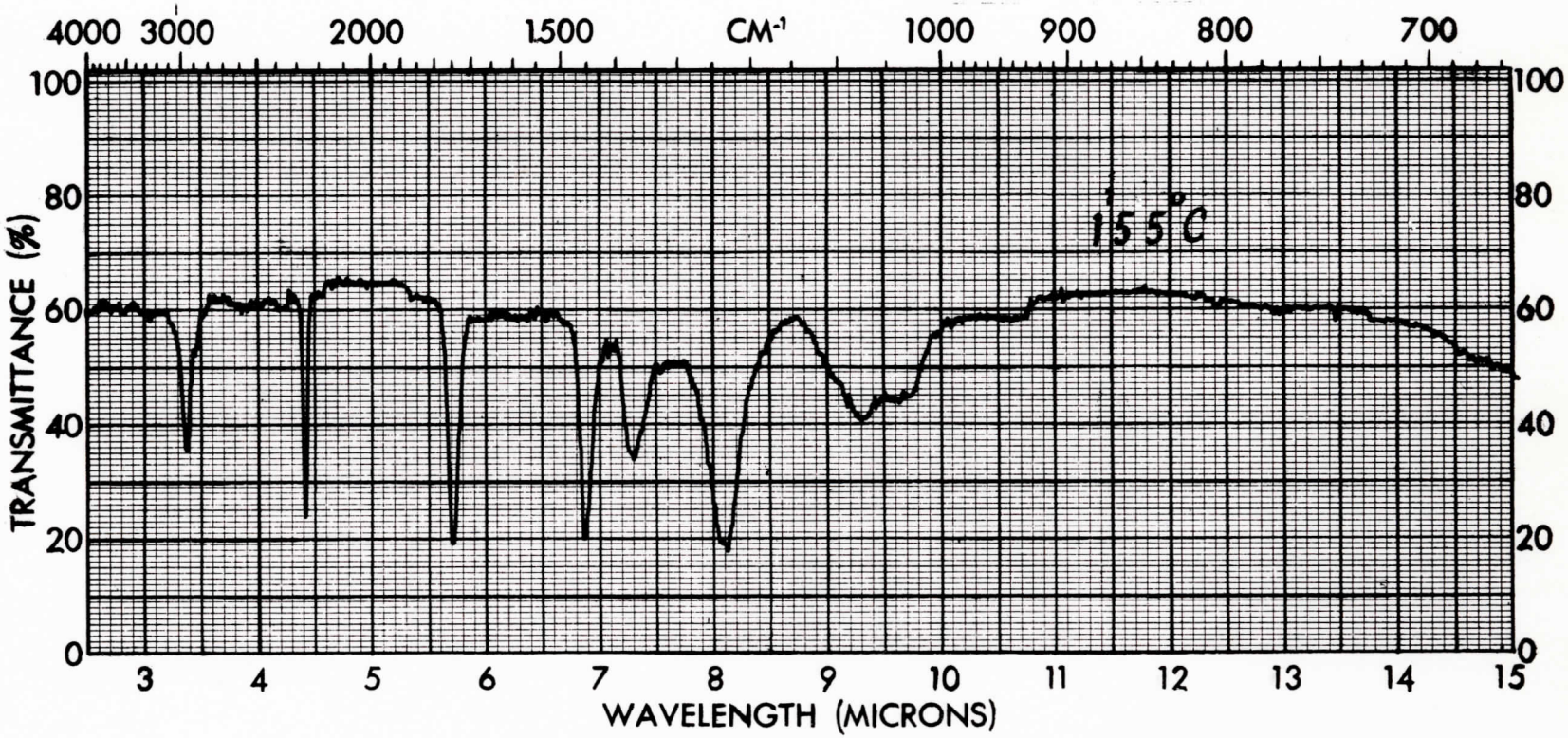


FIGURE 9

THE INFRARED SPECTRUM OF POLYACRYLONITRILE OBTAINED WITH A PERKIN-ELMER INFRACORD, MODEL 137 AT 155°C

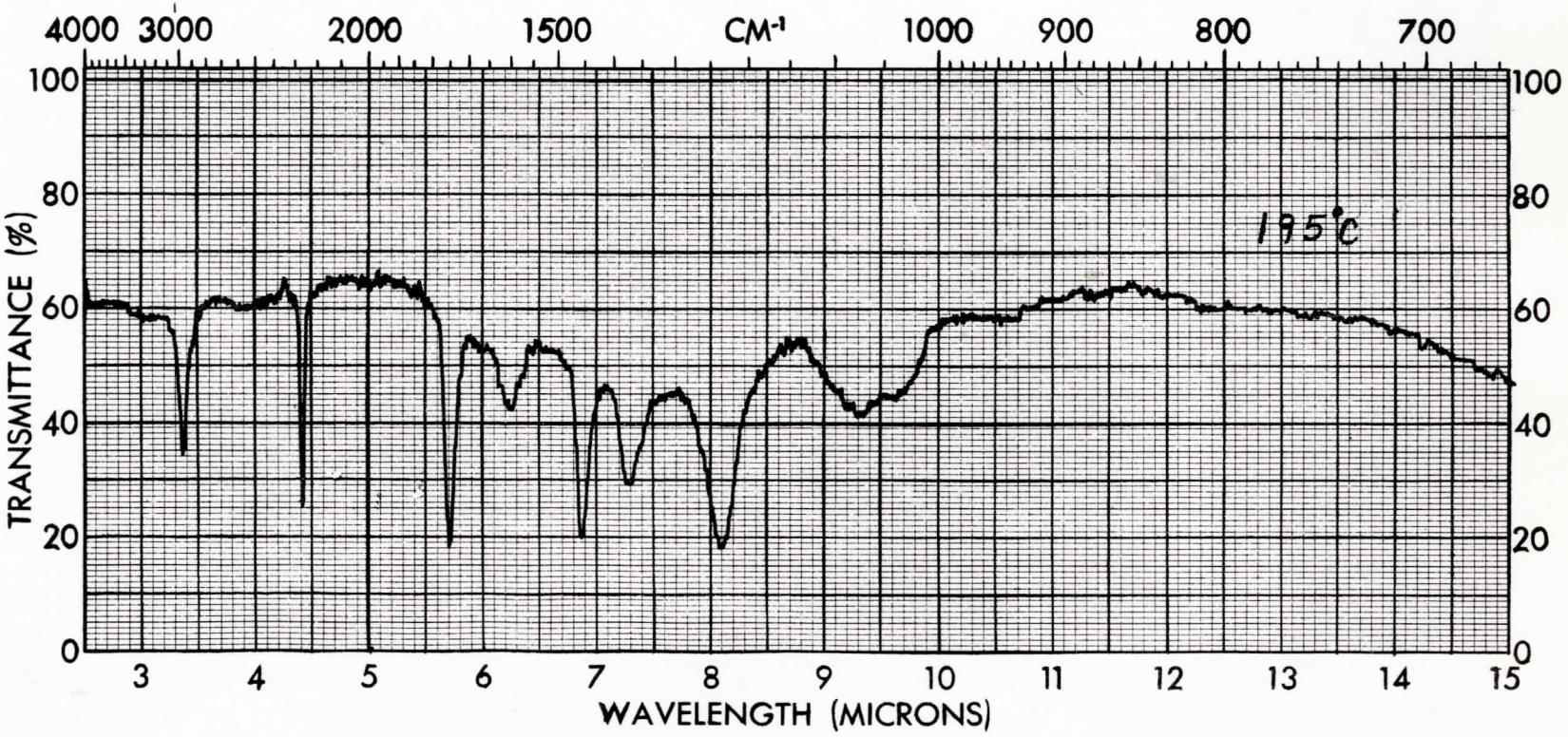


FIGURE 10

THE INFRARED SPECTRUM OF POLYACRYLONITRILE OBTAINED WITH A PERKIN-ELMER INFRACORD, MODEL 137 AT 195°C

This result together with the sorption studies imply that polyacrylonitrile is not a two phase structural system consisting of perfectly ordered regions and perfectly disordered zones. It is, rather, a one phase system consisting of structural elements somewhere in between these two extremes, and partaking of properties of each.

A KINETICS STUDY OF THE SORPTION OF IODINE BY POLYACRYLONITRILE

The preliminary studies of the iodine solutions of ethyl alcohol, carbon tetrachloride, water, and aqueous potassium iodide solution show that no significant amount of iodine was sorbed by the polyacrylonitrile films. However, the films readily sorbed relatively large amounts of iodine at 40°C from the aqueous potassium iodide solution.

It appears from these results, that the sorption process involves the I_3^- ion.

In a more detailed study, it was found that the iodine was sorbed at different rates when placed in I_2-KI solutions of various concentrations. As the concentration increases, the amount of sorption increases rapidly. Therefore, the amount of iodine sorbed by polyacrylonitrile depends on the concentration of the I_2-KI solution. The results of this study are given in Tables III, IV, and V, and are depicted graphically by Figures 11, 12, and 13.

TABLE III

THE PERCENT OF IODINE SORBED BY POLYACRYLONITRILE FILMS FROM I_2-KI SOLUTIONS OF VARIOUS CONCENTRATIONS AT A TEMPERATURE OF 59.7°C AND OVER A PERIOD OF THIRTY MINUTES

Concentration-g/l	Percent Iodine Sorbed
2	0.1
4	0.5
8	1.7
12	8.0
16	23.0
20	45.5
24	63.5

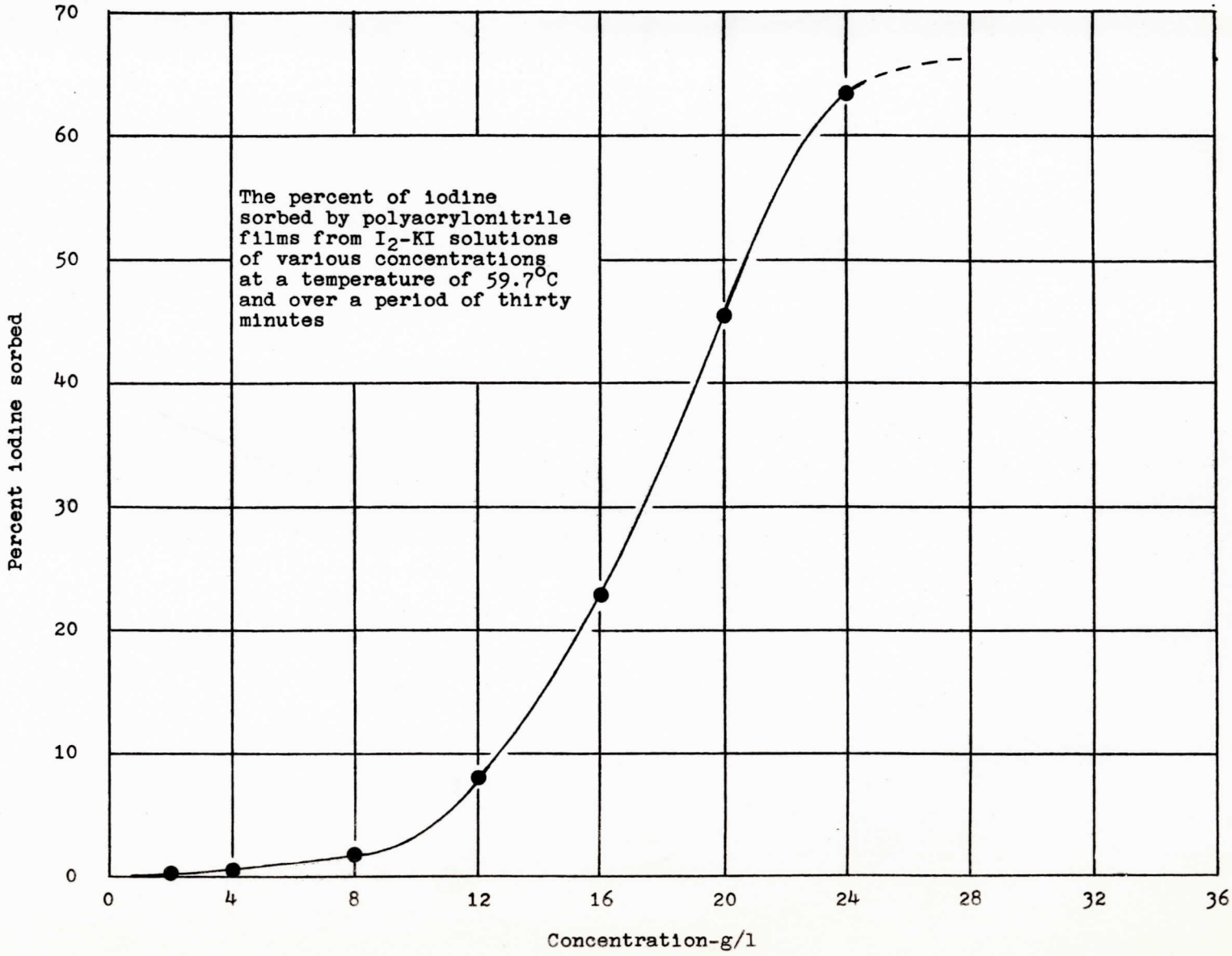

The percent of iodine sorbed by polyacrylonitrile films from I_2-KI solutions of various concentrations at a temperature of 59.7°C and over a period of thirty minutes
Percent iodine sorbed
0
10
20
30
40
50
60
70
0
4
8
12
16
20
24
28
32
36
Concentration-g/l

Figure 11

TABLE IV

THE PERCENT OF IODINE SORBED BY POLYACRYLONITRILE FILMS FROM I_2-KI SOLUTIONS OF VARIOUS CONCENTRATIONS AT A TEMPERATURE OF 59.7°C AND OVER A PERIOD OF ONE HOUR

Concentration-g/l	Percent Iodine Sorbed
0	0.0
2	0.1
4	1.0
8	3.4
12	15.5
16	38.7
20	55.5
24	63.5

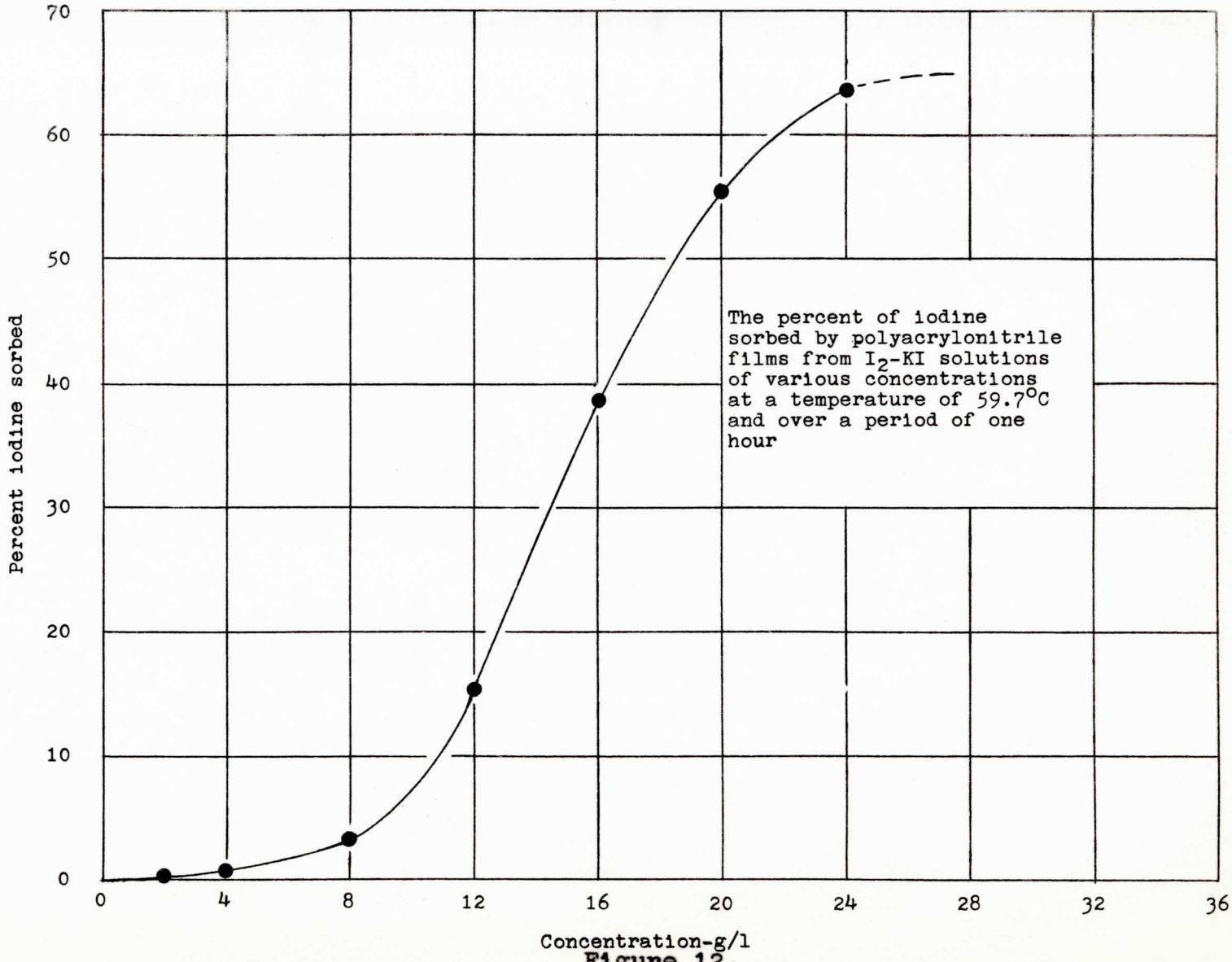

70
60
50
40
30
20
10
0
Percent iodine sorbed
0
4
8
12
16
20
24
28
32
36
Concentration-g/l
The percent of iodine sorbed by polyacrylonitrile films from I_2-KI solutions of various concentrations at a temperature of 59.7°C and over a period of one hour

Figure 12

TABLE V

THE PERCENT OF IODINE SORBED BY POLYACRYLONITRILE FILMS FROM I_2-KI SOLUTIONS OF VARIOUS CONCENTRATIONS AT A TEMPERATURE OF 59.7°C AND OVER A PERIOD OF TWO HOURS

Concentration-g/l	Percent Iodine Sorbed
0	0.0
2	0.2
4	2.0
8	6.3
12	25.7
16	45.0
20	55.5
24	63.5

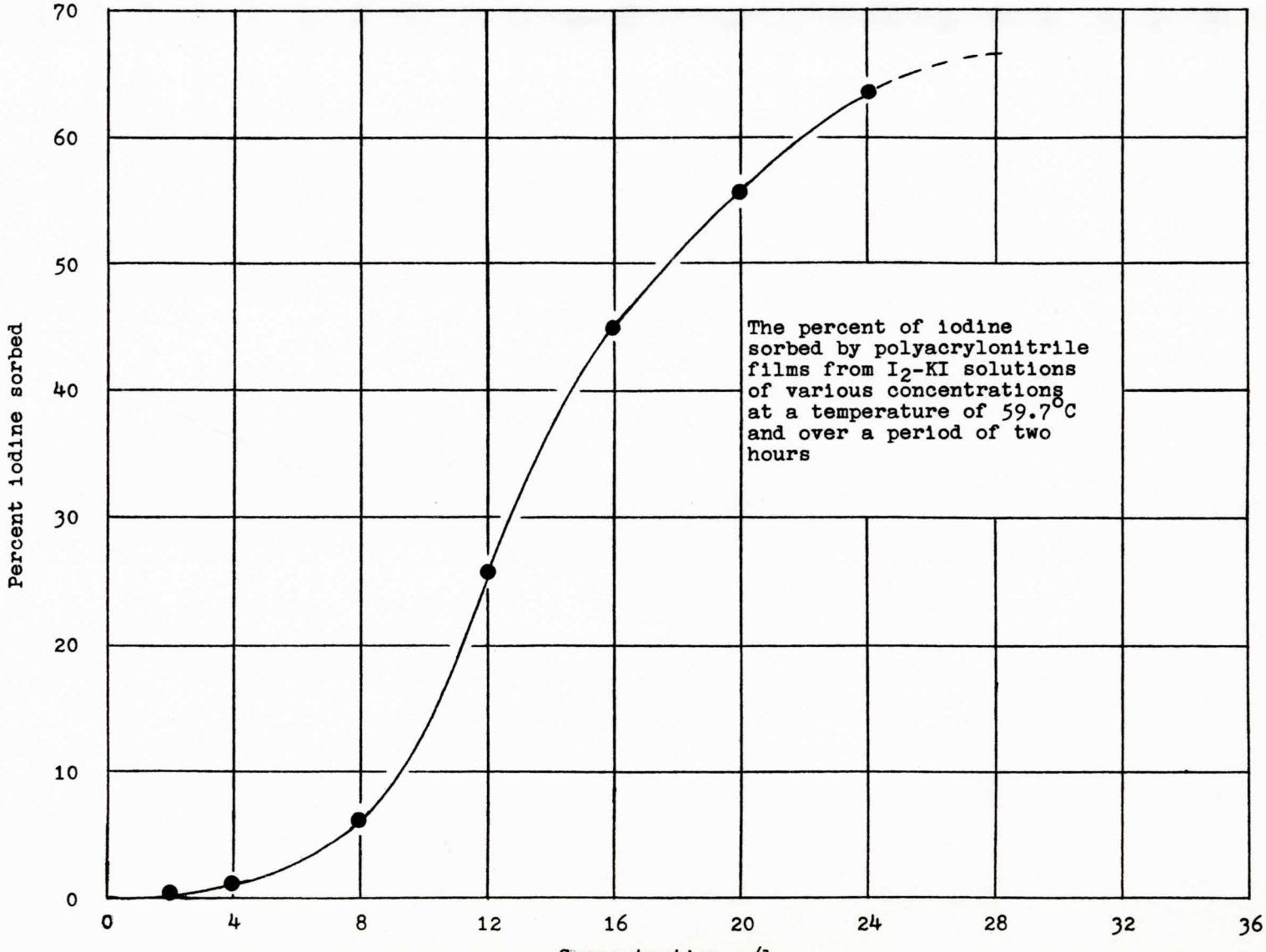

70
60
50
40
30
20
10
0
Percent iodine sorbed
0
4
8
12
16
20
24
28
32
36
Concentration-g/l
The percent of iodine sorbed by polyacrylonitrile films from I_2-KI solutions of various concentrations at a temperature of 59.7°C and over a period of two hours

Figure 13

The next variable to be studied was temperature. At low temperatures the amount of iodine sorbed by polyacrylonitrile films was very small. As the temperature increases, the amount sorbed rapidly increases. The increase in the iodine sorption with the increase in temperature demonstrates the effect of temperature upon iodine sorption by polyacrylonitrile. The results for this study are listed in Tables VI, VII, and VIII, and shown graphically in Figures 14, 15, and 16. Table IX and Figure 17 illustrate the change in the rate of sorption of iodine by films immersed in a solution having a concentration of 20 g/l and over a period of three hours.

The results obtained for the sorption of iodine as a function of concentration and temperature provide information concerning the type of sorption taking place. If it is assumed that the type of sorption is physical, the change in concentration should not alter the rate at which the iodine is taken up. Therefore, it is concluded that the sorption in this case is chemisorption. Also, the increase of temperature should have no effect on the rate of sorption if it were physical. Here, however, the rate of sorption increases rapidly as the temperature increases. Thus, the sorption is activated chemisorption. This is consistent with the fact that the rate of activated chemisorption is sensitive to and dependent upon the energy of the system.

TABLE VI

THE PERCENT OF IODINE SORBED BY POLYACRYLONITRILE FILMS AT VARIOUS TEMPERATURES FROM A I_2-KI SOLUTION HAVING A CONCENTRATION OF 24 g/l AND OVER APERIOD OF TWELVE MINUTES

Temperature	Percent Iodine Sorbed
34.5	0.4
44.3	1.6
49.7	4.1
55.7	16.5
59.7	38.0
65.0	55.0

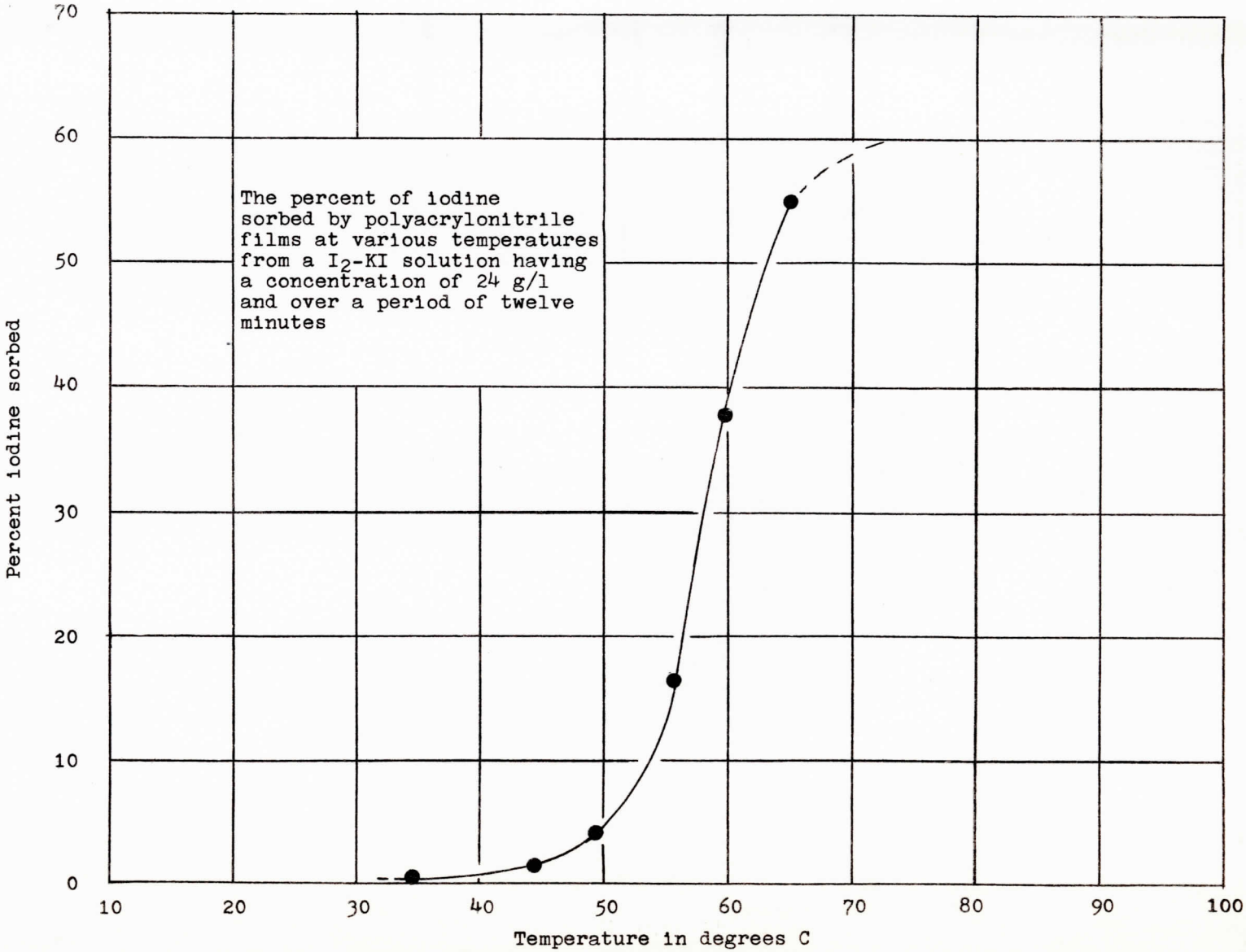

The percent of iodine sorbed by polyacrylonitrile films at various temperatures from a I_2-KI solution having a concentration of 24 g/l and over a period of twelve minutes
Percent iodine sorbed
0
10
20
30
40
50
60
70
10
20
30
40
50
60
70
80
90
100
Temperature in degrees C

Figure 14

TABLE VII

THE PERCENT OF IODINE SORBED BY POLYACRYLONITRILE FILMS AT VARIOUS TEMPERATURES FROM A I_2-KI SOLUTION HAVING A CONCENTRATION OF 20 g/l AND OVER A PERIOD OF TWENTY-FOUR MINUTES

Temperature	Percent Iodine Sorbed
34.5	0.8
44.3	1.0
49.7	4.3
55.7	15.0
59.7	37.0
65.0	49.5

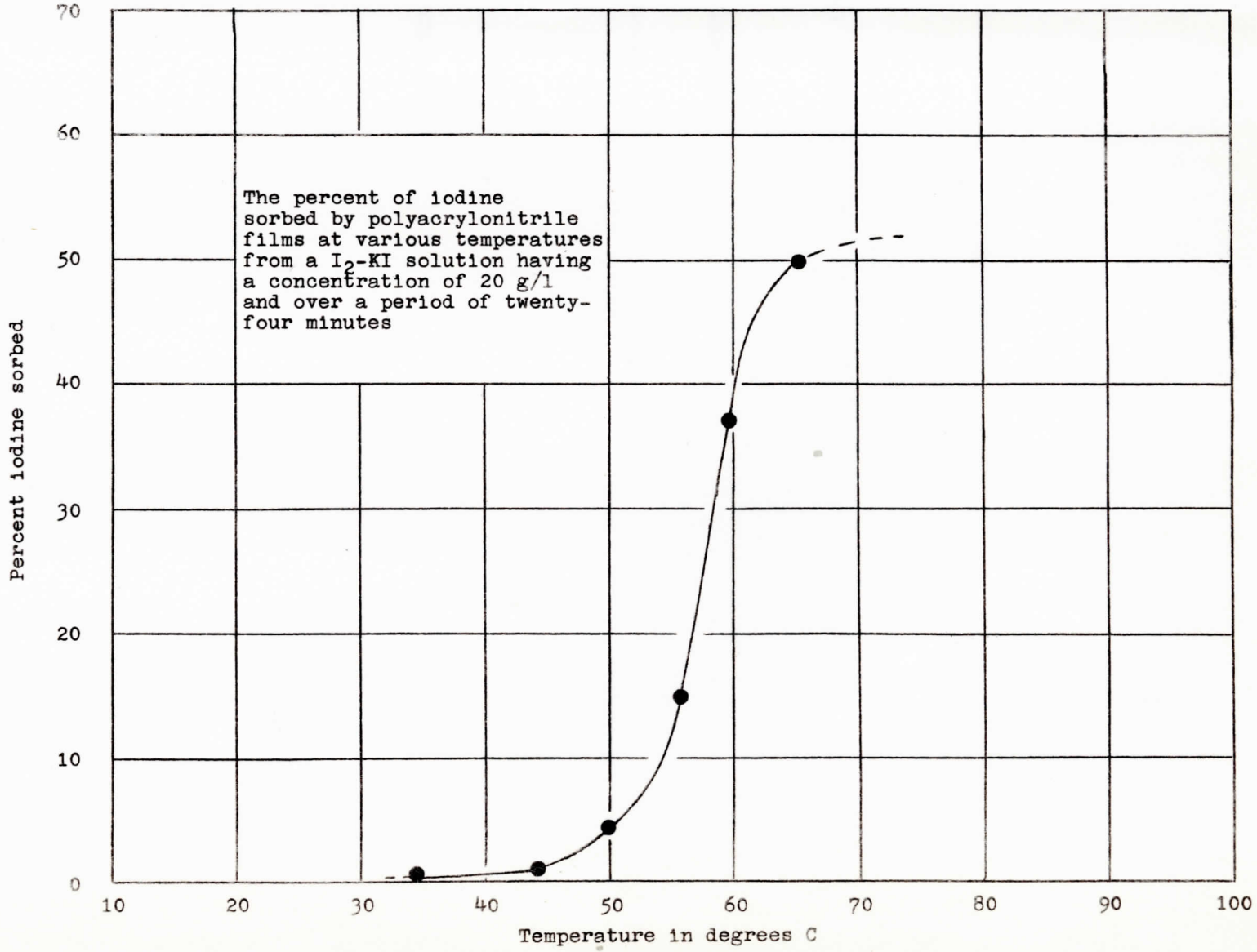

The percent of iodine sorbed by polyacrylonitrile films at various temperatures from a I_2-KI solution having a concentration of 20 g/l and over a period of twenty-four minutes
Percent iodine sorbed
0
10
20
30
40
50
60
70
10
20
30
40
50
60
70
80
90
100
Temperature in degrees C

Figure 15

TABLE VIII

THE PERCENT OF IODINE SORBED BY POLYACRYLONITRILE FILMS AT VARIOUS TEMPERATURES FROM A I_2-KI SOLUTION HAVING A CONCENTRATION OF 20 g/l AND OVER A PERIOD OF THIRTY MINUTES

Temperature	Percent Iodine Sorbed
34.5	1.2
44.3	3.5
49.7	5.5
55.7	19.5
59.7	45.5
65.0	49.5

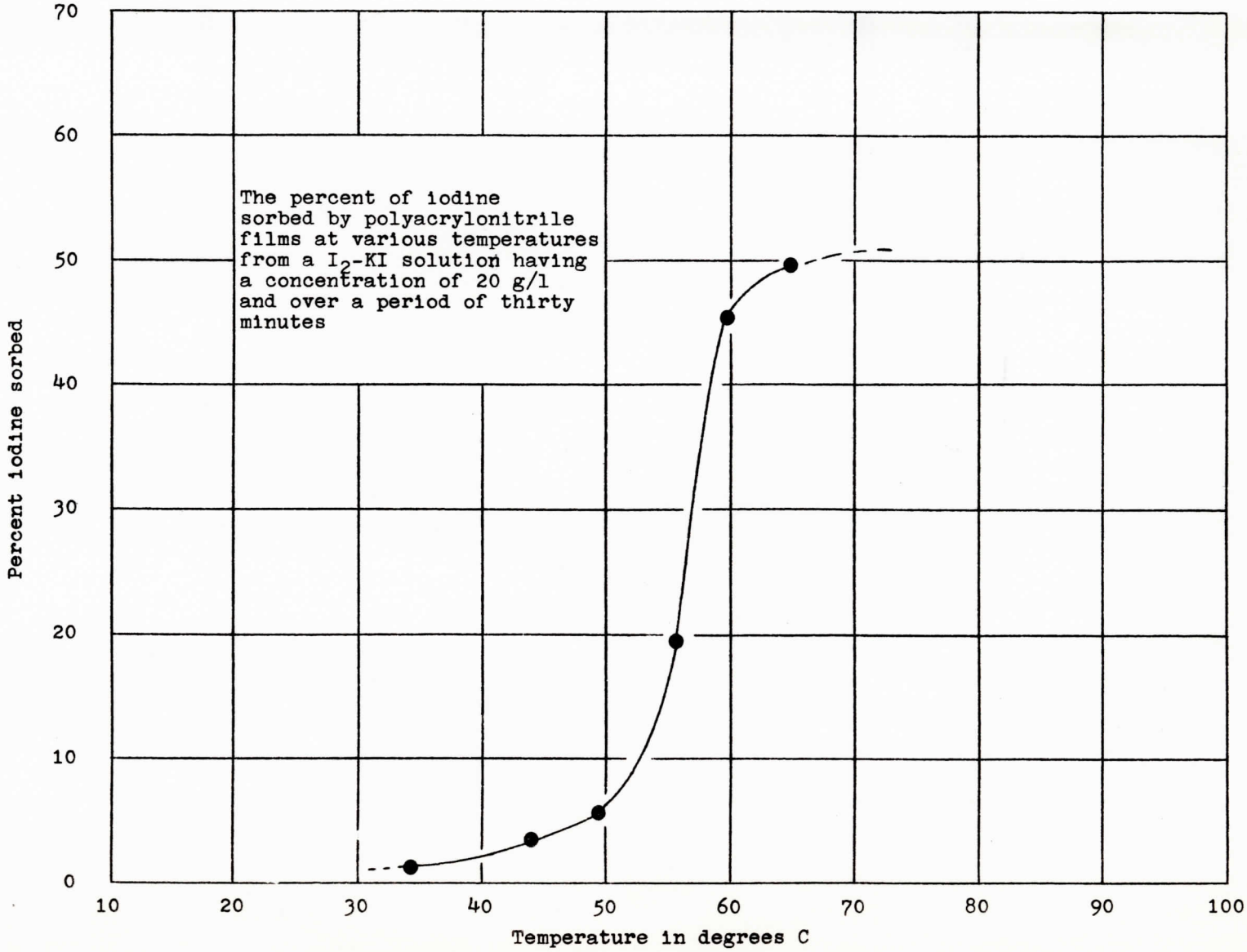

The percent of iodine sorbed by polyacrylonitrile films at various temperatures from a I_2-KI solution having a concentration of 20 g/l and over a period of thirty minutes
Percent iodine sorbed
0
10
20
30
40
50
60
70
10
20
30
40
50
60
70
80
90
100
Temperature in degrees C

Figure 16

TABLE IX

THE PERCENT OF IODINE SORBED AT VARIOUS TEMPERATURES FROM A I_2-KI SOLUTION HAVING A CONCENTRATION OF 20 g/l AND OVER A PERIOD OF THREE HOURS

Temperature	Time In Minutes	Percent Iodine Sorbed
I 44.3°C	60	3.9
I 44.3°C	140	14.2
I 44.3°C	180	17.2
II 49.7°C	60	11.9
II 49.7°C	122	26.2
II 49.7°C	180	38.2
III 55.7°C	15	15.3
III 55.7°C	30	33.9
III 55.7°C	45	45.3
III 55.7°C	75	56.1
III 55.7°C	135	56.1
IV 59.7°C	10	16.1
IV 59.7°C	20	32.2
IV 59.7°C	30	45.5
IV 59.7°C	40	52.7
IV 59.7°C	60	55.4
IV 59.7°C	80	55.4

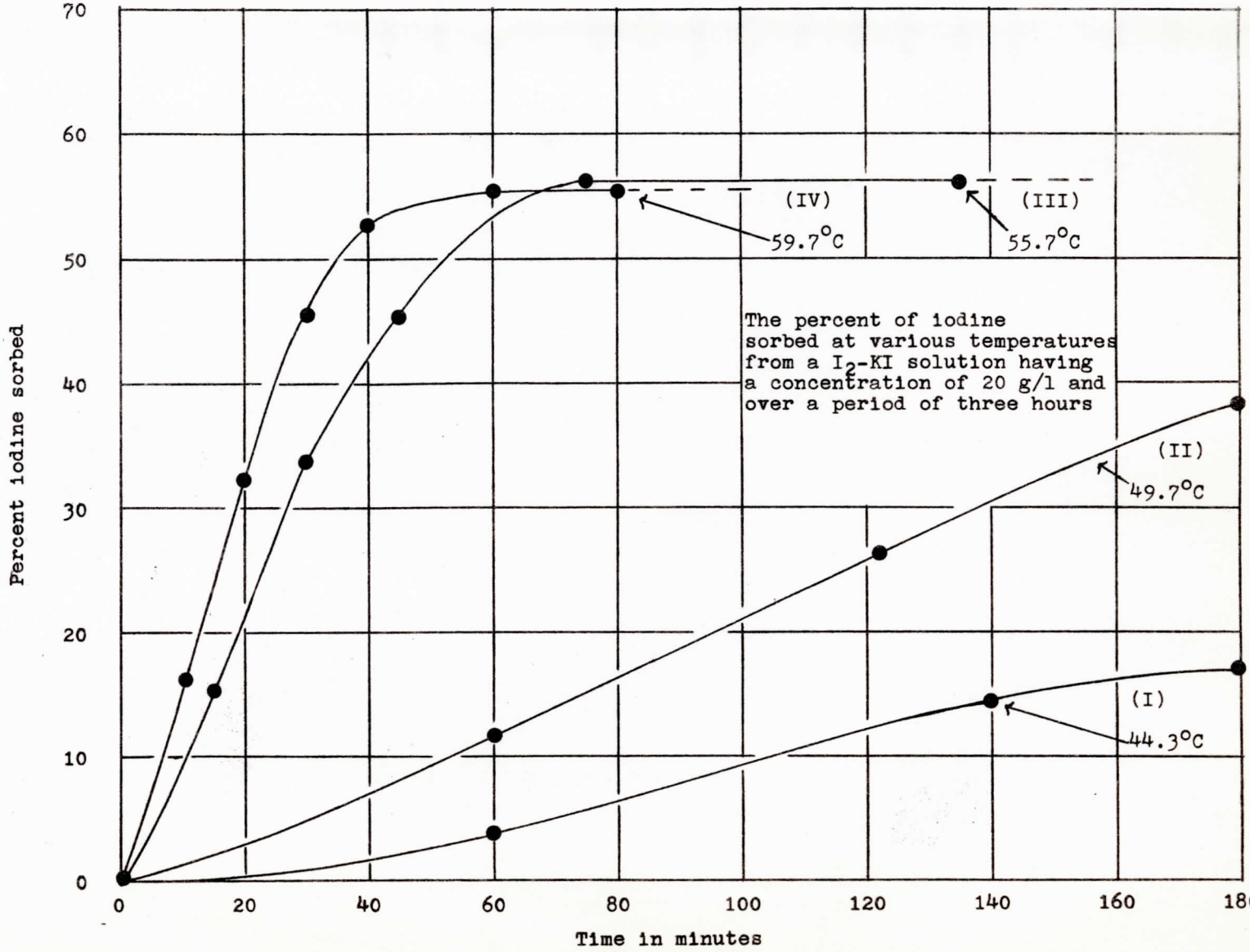

70
60
50
40
30
20
10
0
Percent iodine sorbed
0
20
40
60
80
100
120
140
160
180
Time in minutes
(IV)
59.7°C
(III)
55.7°C
The percent of iodine sorbed at various temperatures from a I_2-KI solution having a concentration of 20 g/l and over a period of three hours
(II)
49.7°C
(I)
44.3°C

Figure 17

Table X and Figure 18 show how the rate of sorption changes with increasing concentration. It is seen from these curves that the rate increases with increasing concentration.

The dependence of the sorption rate also provides evidence for chemisorption. The time necessary for equilibrium to be reached in the sorption process also furnishes information concerning the nature of the film surface. The presence of a large number of holes, crevices, or capillaries tend to extend the time necessary for equilibrium to be reached. When fewer of the pores or deperssions are present, the time necessary for equilibrium to be reached is less. This is due to the slow rate at which the I_3^- ions diffuse into these pores.

When these iodine treated films were studied by means of infrared spectroscopy, no change of the CN absorption band was found. In fact, none of the bands appeared to change.

A STUDY OF THE RATE OF SORPTION OF IODINE BY POLYACRYLONITRILE AS A FUNCTION OF THERMAL TREATMENT

In normal polymers, the density of the polymer may be used as a measure of the order-disorder structure in the polymer. Therefore, by use of thermal and mechanical treatments, one can prepare samples having different densities

TABLE X

THE PERCENT OF IODINE SORBED BY POLYACRYLONITRILE FILMS FROM I_2-KI SOLUTIONS OF VARIOUS CONCENTRATIONS AT A TEMPERATURE OF 55.75°C AND AT VARIOUS TIMES

Concentration In g/l	Time In Minutes	Percent Iodine Sorbed
(I) 16 g/l	0	0.0
(I) 16 g/l	15	3.5
(I) 16 g/l	30	8.1
(I) 16 g/l	45	11.6
(I) 16 g/l	90	26.3
(I) 16 g/l	150	36.6
(II) 20 g/l	0	0.0
(II) 20 g/l	15	8.4
(II) 20 g/l	30	19.6
(II) 20 g/l	45	28.0
(II) 20 g/l	60	37.3
(II) 20 g/l	105	53.0
(II) 20 g/l	165	59.8
(III) 24 g/l	0	0.0
(III) 24 g/l	15	19.9
(III) 24 g/l	30	35.6
(III) 24 g/l	45	50.0
(III) 24 g/l	60	61.0
(III) 24 g/l	75	66.0
(III) 24 g/l	90	69.5
(III) 24 g/l	120	70.0

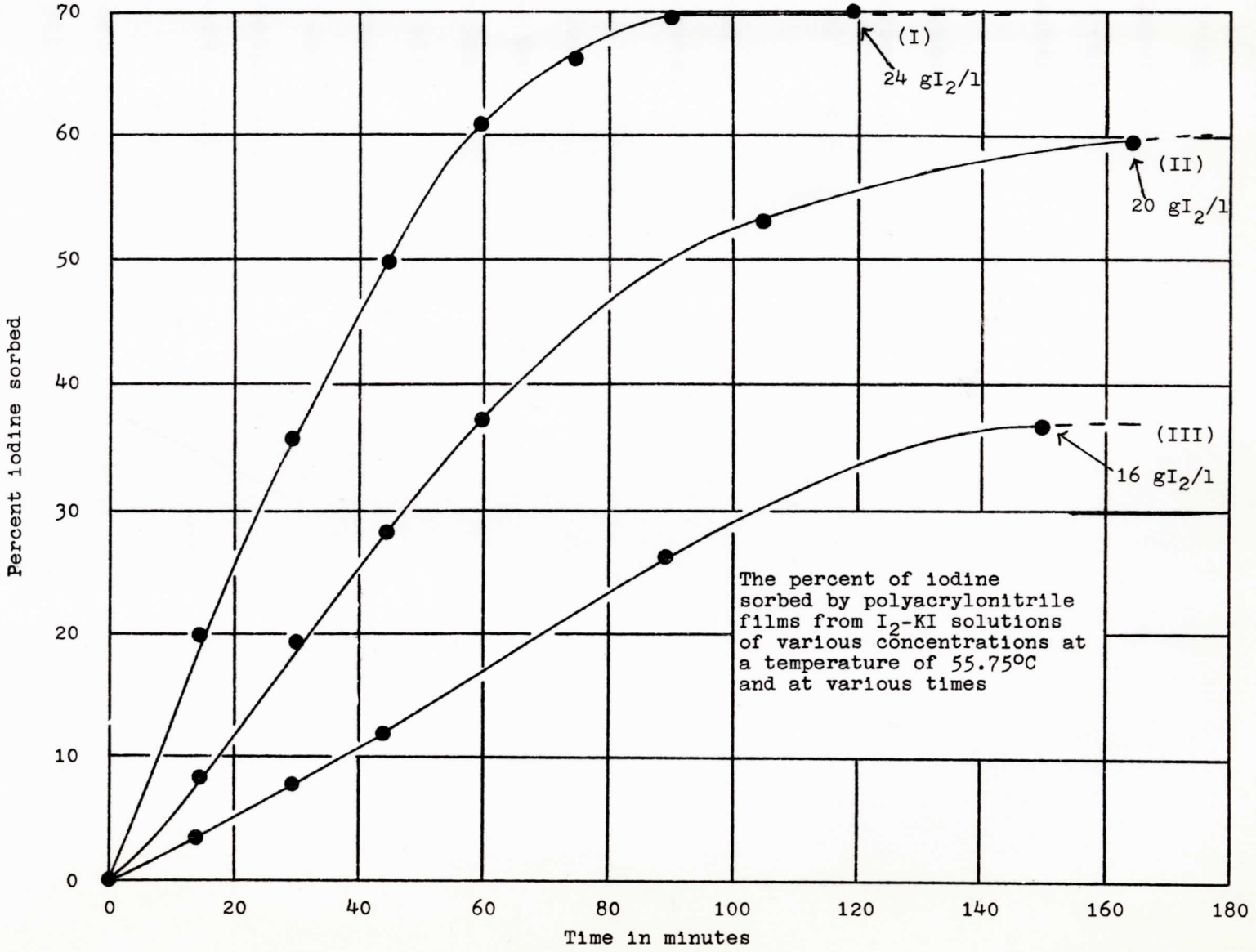

Percent iodine sorbed
70
60
50
40
30
20
10
0
0
20
40
60
80
100
120
140
160
180
Time in minutes
(I)
24 gI2/l
(II)
20 gI2/l
(III)
16 gI2/l
The percent of iodine sorbed by polyacrylonitrile films from I2-KI solutions of various concentrations at a temperature of 55.75°C and at various times

Figure 18

by altering the relative amounts of the ordered and disordered regions of the polymer. Such alterations become important in the normal polymers and may often be demonstrated by the rates of solution and sorption of various materials.

In this study films were prepared by the method described. Heat treatments of the films at various temperatures were given. This treatment gave films having different densities.

In this study, no correlation between the densities and the rate of sorption could be detected. This is illustrated by Table XI and Figure 19.

Analysis of these data gives further support to the idea that the structure of polyacrylonitrile is not consistent with the two-phase system. The increase in density normally reflects an increase in the crystalline regions. A slower rate of sorption of the iodine would be expected. Since the rate of sorption does not exhibit a dependence upon the density, it is suggested that the type of sorption taking place is adsorption. In the case of absorption, the rate would tend to increase as the density decreases.

A total analysis of the sorption of iodine suggests that the process occurring is primarily adsorption, of the activated chemisorption type.

TABLE XI

THE PERCENT OF IODINE SORBED AT VARIOUS TIMES FROM A I_2-KI SOLUTION HAVING A CONCENTRATION OF 20 g/l AND AT A TEMPERATURE OF 55.75°C BY POLYACRYLONITRILE FILMS PREPARED AT DIFFERENT TEMPERATURES

Density	Time In Minutes	Percent Iodine Sorbed
(I) 1.1016	10	15.0
(I) 1.1016	20	30.0
(I) 1.1016	30	42.5
(I) 1.1016	40	51.1
(I) 1.1016	60	56.5
(I) 1.1016	80	57.3
(I) 1.1016	110	57.3
(I) 1.1016	140	57.3
(II) 1.1565	33	28.6
(II) 1.1565	60	45.5
(II) 1.1565	90	53.3
(II) 1.1565	120	53.3
(III) 1.1051	20	11.3
(III) 1.1051	40	20.6
(III) 1.1051	60	32.0
(III) 1.1051	80	39.4
(III) 1.1051	110	46.6
(III) 1.1051	140	50.6
(III) 1.1051	170	52.6

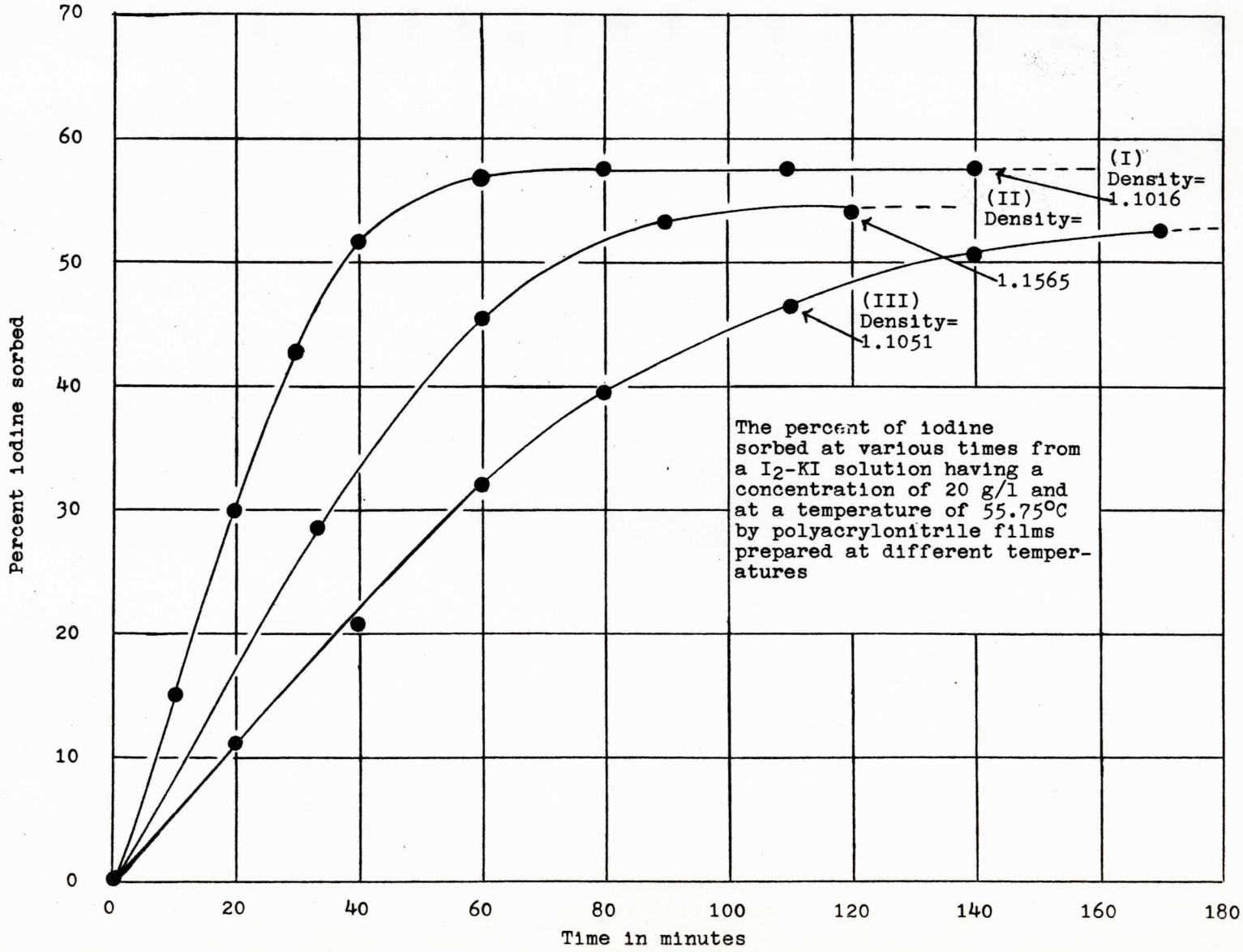

70
60
50
40
30
20
10
0
Percent iodine sorbed
0
20
40
60
80
100
120
140
160
180
Time in minutes
(I)
Density=
1.1016
(II)
Density=
1.1565
(III)
Density=
1.1051
The percent of iodine sorbed at various times from a I_2-KI solution having a concentration of 20 g/l and at a temperature of 55.75°C by polyacrylonitrile films prepared at different temperatures

Figure 19

From a study of Figure 20 (2), one can see a very close similarity between the rate of sorption of copper and acid dye by polyacrylonitrile and the sorption of iodine by the polymer. Thus, it appears that the mechanism of sorption of cuprous ions is one of adsorption, also.

THE DISORIENTING AND SOFTENING OF FIBERS AND FILMS OF POLYACRYLONITRILE BY AQUEOUS KI-I_2 SOLUTIONS

Upon placing fibers and films of polyacrylonitrile in concentrated KI-I_2 solutions at about 100°C, the polymer appeared to soften and partially dissolve.

These results suggest that upon sorption of large amounts of iodine, the polymer tends to relax its conformation. This seems to suggest that the polymer is a single phase system which has very weak intermolecular forces and strong intramolecular forces of the dipolar type. The adsorbed iodine appears to attract the nitrile groups and thus reduce the intramolecular repulsive forces between the nitrile groups along the chain.

It is suggested that this chemisorption is also the mechanism by which polyacrylonitrile is dissolved by such polar compounds as N,N-dimethylformamide and dimethylsulfoxide.

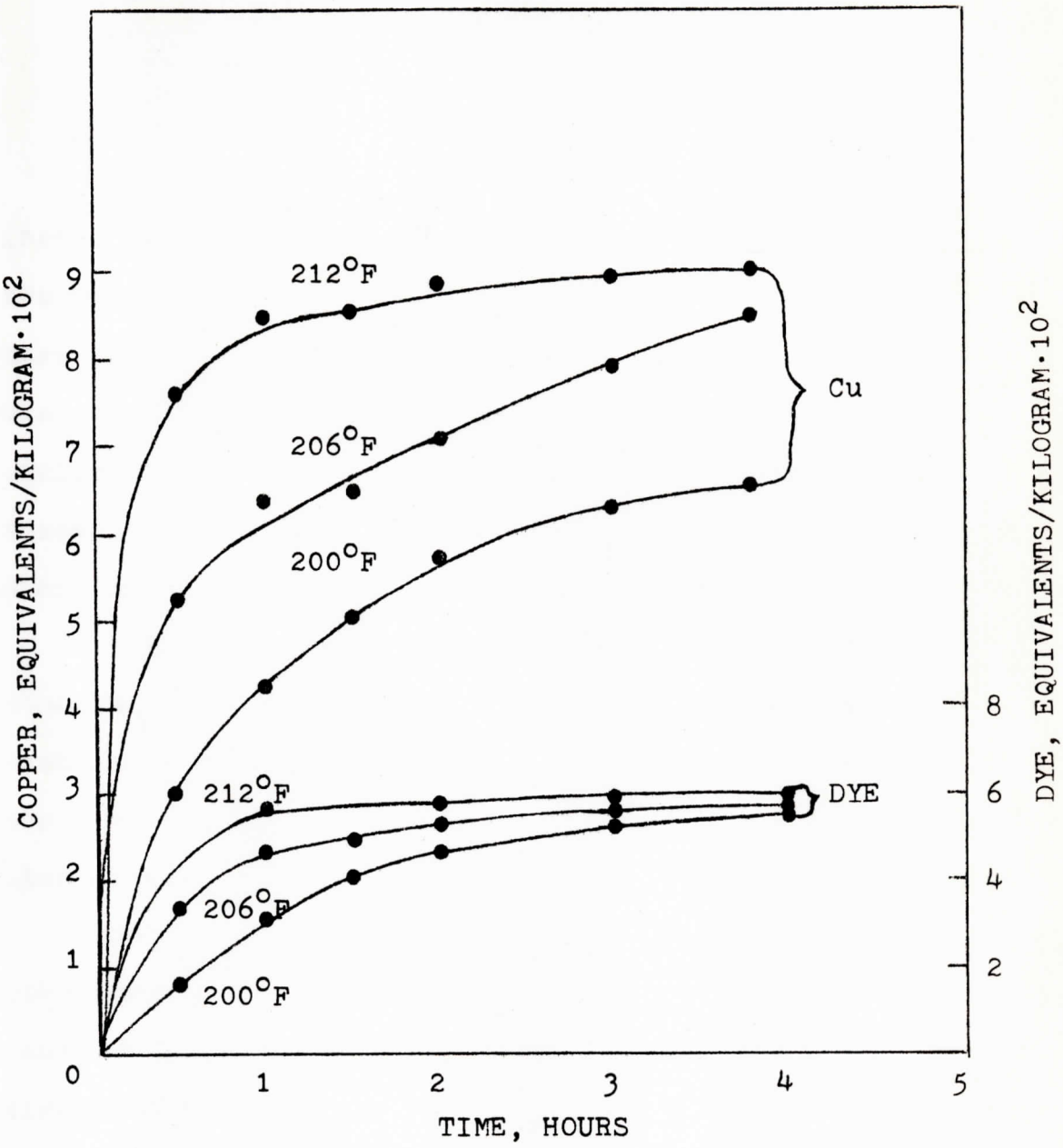


Figure 1
Variation of Rate of Absorption of Copper
and Acid Dye with Temperature

FIGURE 20

CHAPTER V

SUMMARY AND CONCLUSIONS

SUMMARY

A literarure survey of the structure of polyacrylonitrile reveals that two models for the physical structure have been proposed. The earlier model was that of a two-phase crystalline-amorphous structure in which chain molecules were in an extended planar conformation with a regular syndiotactic configuration of the nitrile groups. Adjacent chains were held together laterally by intermolecular forces of the hydrogen bonding type.

A later model is that of a single phase structure in which the order is intermediate between perfectly crystalline and completely disordered. Chains are distorted into a randomly kinked conformation due to the intramolecular dipolar repulsions of the nitrile groups.

Detailed investigations of the sorption of N,N-dimethylformamide by oriented fibers of polyacrylonitrile by means of light microscopy are reported. A decrease of filament diameter is observed. Together with this, fibers immersed in alcoholic and aqueous mixtures of N,N-dimethylformamide show no uptake of dimethylformamide by refractive index measurments. Also, films of polyacrylonitrile, treated in this way, give a similar result by refractive index

measurments. The infrared spectra of these films show no significant appearance of the amide stretching frequency, 1675 cm^{-1}, for the dimethylformamide.

In addition, infrared spectra of polyacrylonitrile films were obtained at constant temperatures ranging from 30°C to 200°C. These spectra, ranging from 700 cm^{-1} to 4000 cm^{-1}, were obtained with a Perkin-Elmer heated cell used in association with both a Perkin-Elmer Infracord, Model 137, and a Beckmann Infrared Spectrophotometer, IR-7. The CH_2 stretching, 2940 cm^{-1}; CN stretching, 2275 cm^{-1}; and the CH_2 bending, 1450 cm^{-1}, frequencies show no significant changes in either position or intensity.

The infrared absorption band for the CH stretching frequency was obtained with the Beckmann IR-7 Infrared Spectrophotometer for a polyacrylonitrile film, and a solution of polyacrylonitrile in dimethylformamide. The frequency, 2243 cm^{-1}, is not shifted significantly for the solution over that of the film.

Finally, a detailed study of the sorption of iodine by polyacrylonitrile films was made. In this study, films were immersed in alcoholic iodine mixtures, mixtures of iodine in carbon tetrachloride, and mixtures of iodine in aqueous potassium iodide solutions at temperatures between 30°C and 60°C, and over periods of time ranging from thirty minutes to forty-eight hours. Significant amounts of iodine are sorbed only from the aqueous potassium iodide solutions.

Also, oriented fibers immersed in the aqueous potassium iodide-iodine solutions partially dissolve at 97°C. In addition, the infrared absorption frequency of the CN stretch of the iodine treated films show no significant change.

The sorption of iodine was investigated as a function of concentration, and temperature. The amount of sorption increases with increasing concentration and also increasing temperature.

Finally, the rate of sorption was investigated as a function of density. The rates differ, but can not be correlated with the density differences. The time necessary to obtain equilibrium is relatively long, indicating depressions or microvoids in the film surface.

These results are consistent with the single phase physical structure recently proposed by Bohn, Statton, et. al. (3).

CONCLUSIONS

It is concluded from these studies that intermolecular hydrogen bonding in polyacrylonitrile does not exist to any appreciable extent. Also, the sorption and thermal treatments are in agreement with the single phase structure recently proposed (3). In addition, it is proposed that polyacrylonitrile films sorb iodine by a process of multilayer activated chemisorption which involves the I_3^- ion

dipole. Finally, it is suggested from these studies that the copper dyeing of orlon and the solubility of polyacrylonitrile in N,N-dimethylformamide and other polar solvents proceeds by way of this chemisorption mechanism.

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